PB-212 859

AN IMPROVED MANUAL METHOD FOR NOx EMISSION MEASUREMENT

L. A. Dee, et al

Air Force Rocket Propulsion Laboratory

Prepared for:

Environmental Protection Agency

October 1972

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EPA-R2-72-067
October 1972

PB 212 859

Environmental Protection Technology

EPA-R2-72-067 An Improved Manual Method for NO_x Emission Measurement

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Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington,D.C. 20460

167

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-R2-72-067	2.	3. Recipient's Accession No.
4. Title and Subtitle: An Improved Manual Method for NO_x Emission Measurement			5. Report Date: October 1972 6.
7. Author(s): L.A. Dee, H.H. Martens, C.I. Merrill, et al			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: Air Force Rocket Propulsion Laboratory Air Force Systems Command United States Air Force Edwards, California			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address: U. S. ENVIRONMENTAL PROTECTION AGENCY Office of Research and Monitoring Washington, D. C. 20460			13. Type of Report & Period Covered 14.

15. Supplementary Notes

16. Abstracts

The current manual NO_x sampling and analysis method was evaluated. Improved time-integrated sampling and rapid analysis methods were developed. In the new method, the sample gas is drawn through a heated bed of uniquely active, crystalline, PbO_2 where NO_x is quantitatively absorbed. Nitrate ion is later extracted with water and the concentration subsequently determined by a NO_3^- Selective Ion Electrode. A simple selective precipitation eliminates electrode interferences derived from PbO_2 absorption of other combustion products such as HCl, SO_x, HF, and CO. Field tests were conducted at various stationary source sites and the data is presented herein.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution
Nitrogen oxides
Sampling
Gas sampling
Chemical analysis
Evaluation
Tests
Field tests

17b. Identifiers/Open-Ended Terms

Stationary sources
Manual method

17c. COSATI Field/Group 13B I-A

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Unlimited	UNCLASSIFIED	107
	20. Security Class (This Page) UNCLASSIFIED	22. Price $3.00

FORM NTIS-35 (REV. 3-72) THIS FORM MAY BE REPRODUCED USCOMM-DC 14952-P72

EPA-R2-72-067

AN IMPROVED MANUAL METHOD FOR NO_x EMISSION MEASUREMENT

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OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460

I-B

October 1972

EPA REVIEW NOTICE

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

Accurate determination of nitrogen oxide (NO_x) emissions from stationary combustion sources is necessary if the Environmental Protection Agency and the various Regional Air Quality Basin Agencies are to set realistic NO_x limits. Furthermore the sampling and analysis technique must be able to pass legal scrutiny by possessing unique technical attributes, should a challenge occur.

The basic problems hampering the currently used NO_x methods are an inherently nonrepresentative sampling technique and an inaccurate analysis method at the projected NO_x emission limits. These disadvantages are aggravated by the fact that the presence of chloride ion also causes erroneously low results in the NO_x analysis method. Chloride is present in many combustion sources.

This report describes the development of a unique manual sampling and analysis method for NO_x from stationary sources. The recommended system has none of the previously cited deficiencies and in addition provides for time integrated sampling and a rapid accurate analysis of the resultant aqueous solution. The acquisition of NO_x data could also be performed in the field without return to a laboratory if necessary. This work was performed during FY 72 at the Air Force Rocket Propulsion Laboratory under Project EPA000CX at the request of and funded by the Environmental Protection Agency. The AFRPL has an interest, in that it too needs accurate information on nitrogen oxide emissions at its facilities because such compounds are both rocket propellants and engine exhaust products.

Mr. F. C. Jaye of the Chemistry and Physics Div. was the EPA Project Engineer.

The laboratory assistance of Mr. M. F. Citro and Mr. B. Dixon is gratefully acknowledged.

This Technical Report has been Reviewed and is Approved.

Paul J. Daily

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I - INTRODUCTION

Approximately sixty percent (60%) of the total United States' emissions of oxides of nitrogen, NO_x ($NO + NO_2$) are derived from fossil fuel burning stationary sources. The quantities involved were estimated to be about 9.6×10^6 tons in 1968 according to Esso Research and Engineering Co. (1). The levels of NO_x in stack gases are reported to range from 20 ppm (v/v) for small gas fired boilers to 1400 ppm (v/v) for coal fired power plants (2). Regulatory agencies on the federal and state or regional levels are projecting the establishment of successively lower NO_x emission limits. Such lower limits will require improvements in the accuracy and sensitivity of current sampling and analysis methods. This need for an improved manual sampling and analysis method for NO_x became urgent as a result of Congressional mandate to set stationary source performance standards. The current NO_x method (3) suffers from numerous disadvantages, the most serious of which is a loss of accuracy in the 100 ppm to 200 ppm range. This single characteristic can have a deleterious effect on possible future legal actions which may be initiated by enforcement agencies. At the request of the Environmental Protection Agency, and based on recommendations and conclusions contained in the Walden Research Corp. Report (2), members of the Rocket Propulsion Laboratory Chemical and Materials Branch investigated and concluded that it was feasible to develop an improved sampling device for stationary emissions coupled with a less tedious and more accurate NO_x analysis.

In the current method (3) an evacuated 2 liter glass flask is attached to a gas sampling apparatus and filled in 0.1 to 0.2 minute to the source pressure. A small amount of absorbing solution oxidizes

the nitric oxide (NO) to the dioxide (NO_2) which in turn reacts with the oxidizing solution to form nitrate ion (NO_3^-), a process which takes up to 16 hours. This type of sample, however, represents an instantaneous point in time and unless the emitting source is constant, the calculated total hourly or daily NO_x emission can be in serious error. Relatively few stationary combustion sources are sufficiently constant for the acquisition of an accurate grab sample.

The sampling time can be lengthened by using a liquid absorbing solution and slowly bubbling a known amount of gas through it, or by use of a solid absorber/reactor which forms solid products with the NO + NO_2 contained in the sample gas stream. This latter possibility appeared quite feasible as a result of the work of Mishmash and Meloan (4) who presented evidence for the quantitative reaction of lead dioxide (PbO_2) with NO and NO_2 at reaction temperatures from 40°C to 190°C to give solid lead nitrate ($Pb(NO_3)_2$). The $Pb(NO_3)_2$ is quite soluble in aqueous solutions when compared to lead compounds formed with other possible combustion gases, such as sulfur dioxide (SO_2), hydrogen chloride (HCl), hydrogen fluoride (HF), and carbon monoxide (CO). Carbon dioxide (CO_2), also a combustion product, does not react with PbO_2 according to Pregl (5).

Other approaches to time-integrated sampling were investigated, using liquids in conjunction with ozone, electrolysis, or chemical oxidizers including charge transfer agents (6), but none of these effectively modified the insolubility of NO in an aqueous system. In addition, the lack of quantitative conversion of NO to NO_2 in the presence of other reactive stack gases was responsible for abandoning liquid systems as sampling devices. It should be recalled that the NO_x in combustion stack

gases is generally 95^+ % NO (2) even with air in slight excess.

A preliminary experiment with NO confirmed the quantitative absorption with PbO_2 as reported by Mishmash (4) and also showed that NO_3^- was released when the PbO_2 was washed with distilled water. Variability in PbO_2 reactivity to NO was encountered but was found to be due to sources of PbO_2, or more properly its physical state, as sold by various vendors. The literature (7-9) revealed much controversy over "capacity" or "reactivity" with NO or NO_2 during some 60 years prior to 1969. It appears that of the four distinct forms of PbO_2 only the crystalline α- and β-PbO_2, or a mixture of the two, will yield quantitative recovery with NO.

The determination of NO_3^- in aqueous solutions is well known (3, 10, 11) and efforts to improve the accuracy were carried forward concurrently with the development of the PbO_2 sampling device. The difficulties consisted primarily in minimizing or eliminating the anticipated interferences to the phenoldisulfonic acid (PDS) and the NO_3^- selective ion electrode (SIE) methods. For example, a coal burning power plant will emit HCl and CO which react with PbO_2 to yield $PbCl_2$ and $PbCO_3$. The presence of Cl^- or CO_3^{2-} in solution will cause inaccuracies in the NO_3^- response of the SIE. Similarly Cl^- will interfere with the PDS method (12) and cause erroneously low results. It was discovered that the SIE was even sensitive to changes in pH (hydrogen ion concentration) and was utterly useless in solutions containing peroxide (H_2O_2).

Nevertheless, the work described in the following sections resulted in the development of a time-integrated manual sampling device coupled with two accurate analysis methods for NO_3^-. The system was field tested

and appears satisfactory for NO_x emission measurement of stationary sources above 20 ppm NO_x. Its applicability to mobile sources and the measurement of ambient air NO_x levels also appears possible.

II TECHNICAL DISCUSSION

1.0 Sampling Methods

1.1 Flask Grab Sample Method

The most advantageous feature of the grab sampling method is that the only portable equipment required for its use is an evacuated and calibrated vessel containing a measured volume of gas absorption reagent.

To collect a sample, the flask is connected to a sample port and the flask closure is opened to admit the gas sample. The operation can take as little as ten seconds to accomplish. Following collection, the sample is returned to the laboratory for a final sample pressure measurement and analysis of the absorbing reagent in the flask for the specie of interest. The NO_x method described in the Federal Register (3) is a modified version of the grab sampling technique. The exceptions are that the recommended sampling apparatus includes a vacuum pump for evacuating the flask and a manometer for sampling pressure measurement.

The major disadvantage of the grab sampling technique is that the indicated emission level from any single sample can only represent the value for that brief period of time required to take the sample. Since most emission levels fluctuate due to combustion variations or stack gas turbulence, many grab samples must be taken and the results averaged for accurate daily emission data. Typical NO_x emission data from a stationary diesel engine is shown on Table I. The ten grab samples were randomly spaced during a two-hour sampling period, and the analyses were performed using the PDS method described in sections 2.2 and 3.3.

Table I, Diesel Engine NO_x Data Grab Samples Analyzed by PDS Method.

Sample No.	NO_x (ppm)	Sample No.	NO_x (ppm)
1-3	353	3-5	382
1-5	318	4-3	364
2-1	454	4-5	339
2-2	353	5-1	411
3-1	398	5-2	346

range = 318 to 454 ppm = 136 ppm NO_x

Even though this engine was operating at constant load, it is apparent that a prohibitively large number of grab samples must be taken to accurately show the twenty-four hour average NO_x emission level of this combustion source. For other combustion sources where the fuel feed rate is less carefully controlled, the emission level can be expected to vary even more widely.

1.2 Flask Extended Grab Sample Method

To integrate or average NO_x emission level variations the gas sampling time can be extended by installing a flow restrictor between the flask and the sample point. This idea was investigated using a laboratory NO_x source ($\sim$ 200 ppm NO in N_2). The restrictor was constructed of glass and provided an extended fill time of approximately 12 minutes for the 2 liter flask. No detectable NO_x analysis variation occurred which could be attributed to the use of this extended grab sample technique. Although the method showed promise when laboratory NO sources were sampled, it can be readily seen that this method is doomed to failure for most combustion sources. Because the restrictor must be located between the sample point and the 2-ℓ flask and also must be of very small diameter

(i.e., ~ 0.002 inch) particulate matter or even water mist can plug the opening and thus preclude obtaining a representative sample.

1.3 Time-Integrated Sample Method

A more reliable means of obtaining a daily emission level for NO_x is to collect a sample of the combustion gas at a constant rate for some finite fraction of the emission period of interest. Samples collected by this method, when analyzed, can be related directly to the average emission level. The most important prerequisite for this sampling technique is that the collection medium used will quantitatively trap the species of interest. Thermodynamic studies (1) of combustion systems which use air as the oxidizer have shown that the primary NO_x species formed is nitric oxide (NO). NO is a relatively inert oxide of nitrogen with only limited solubility in liquids. Collection of NO in gas streams using aqueous scrubber systems has been an almost total failure. Several attempts to absorb NO in aqueous media were made during this program.

1.3.1 Gas Phase Pre-oxidation of NO.

Aqueous alkaline o-methoxyphenol has been reported to quantitatively absorb NO_2 (6) and therefore if oxidation of NO to NO_2 can be accomplished readily then absorption in this medium is possible. Attempts to oxidize NO with O_2 and U.V. light or with O_3 resulted in either no reaction at all or in the decomposition of the o-methoxyphenol. In a third attempt to enhance the oxidative process, o-methoxyphenol was prepared in alkaline 10% H_2O_2 solution. Use of the absorption medium resulted in NO recovery which was only 30% of theoretical.

1.3.2 Electrolytic Oxidation of NO.

Anodic oxidation of NO to NO_3^- appeared to be another

means of time-integrated collection. A device was constructed in such a manner that the gas containing NO would directly contact a positively charged porous screen immersed in an aqueous alkaline solution. Later the voltage was increased in order to generate oxygen at the anodic absorption surface. Neither system resulted in greater than 30% recovery of NO.

1.3.3 Solid Absorbants

The Walden Research Corp. reports (2) describe several potential solid sorbents for NO_x and SO_x such as MnO_2, $K_2Cr_2O_7$ and PbO_2 which may be used in time-integrated samplers. Of these solids, PbO_2 appeared to be the most promising since it has a long history of successful application as an NO_2 absorbent in the classical Pregl combustion train. Initial NO recovery tests using PbO_2 were promising. PbO_2, which had been purchased from Fisher Chemical Co. approximately ten years ago, was packed into glass 1/4 in. O.D. x 12 in. tubes and the ends were plugged with glass wool. The Fisher product was certified to be prepared according to Pregl (5) which means that the PbO_2 was digested in concentrated HNO_3, washed with water until NO_3^- free, dried, sieved, and the 12/20 mesh particles retained. Table II shows the NO recovery results from PbO_2 tubes when an unverified 200 ppm NO source was sampled.

Table II, NO Recovery Using the PbO_2 Tube with $\sim$ 200 ppm NO/N_2

Test No.	ppm NO (found)
1	178
2	220
3	145
4	135
$\bar{X}$ =	170

The Table II analysis results show an unacceptable degree of scatter and seem to contain a negative bias of ∿ 15%. Analysis was performed for NO_3^- using the Orion Nitrate Selective Ion Electrode (SIE) in the aqueous PbO_2 slurry. Minor refinement of the method resulted in somewhat better results shown in Table III when a verified 256 ppm NO/He source (see section 2.1) was used.

Table III, NO Recovery Using the PbO_2 Tube with 256 ppm NO/He

Test No.	ppm NO (found)
1	245
2	234
3	236
4	216
5	229
6	238
7	241
$\bar{X}$ =	234

The scatter and negative bias (∿ 9%) are significantly less than the earlier results. The PbO_2 tube sampling method looked very promising and a detailed investigation of the method followed. A second batch of PbO_2 (prepared according to Pregl) was purchased from Matheson Coleman and Bell (MCB) to conduct the more detailed study. We observed that the average particle size of this PbO_2 was somewhat greater than that of the Fisher's but both were used in the "as received" condition. A large quantity of 211 ppm NO/N_2 was prepared to eliminate source variability from the sum of the analytical errors. Table IV shows the comparative results obtained with the modified PDS method and flask (see section 2.2) and the

MCB PbO_2 using the 211 ppm NO source.

Table IV, NO Recovery Using the 211 ppmNO/N_2 Source

Test No.	ppm NO (found)	
	PDS(flask)	MCB PbO_2
1	197	25
2	197	23
3	197	56
4	197	29

The extremely low recovery indicated with this PbO_2 was surprising since both sources (MCB and Fisher) were specially prepared for use in the Pregl combustion train. Mishmash and Meloan (4) reported that $Pb(NO_3)_2$ was formed when NO reacts with PbO_2. Therefore in order to determine if the capacity of the coarser mesh MCB PbO_2 has been exceeded, x-ray diffraction analyses were performed on the inlet and exit sides of a used MCB PbO_2 tube. Traces of $Pb(NO_3)_2$ were detected at the exit end of the tube thus indicating that the capacity had been exceeded. In addition, a used Fisher PbO_2 tube was subjected to the same analysis, since slightly low recovery is also indicated. No $Pb(NO_3)_2$ was detected at the exit end of the tube. However significant differences between the PbO_2 spectra were observed. Figure 1 represents the x-ray diffraction spectra of Fisher and MCB PbO_2. According to x-ray diffraction data (15) PbO_2 can exist in three crystal forms. Table V depicts the crystal form composition of the two batches of PbO_2 (assuming that no amorphous materials are present and that the sensitivities of the three forms are equal).

Figure 1

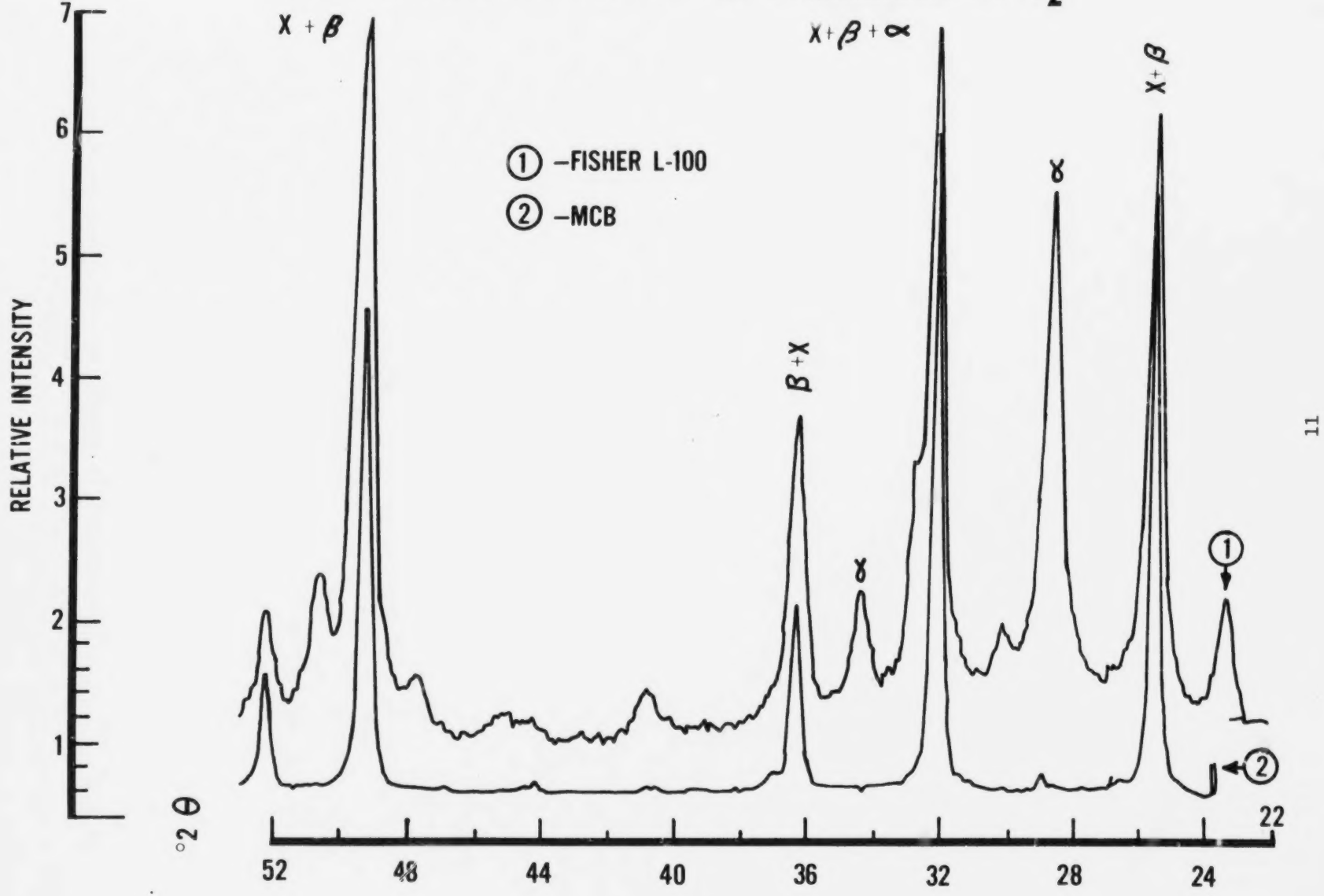

X-RAY DIFFRACTION SPECTRA OF COMMERCIAL Pb O_2
RELATIVE INTENSITY
7
6
5
4
3
2
1
X + β
X+β+α
X+β
β+X
γ
γ
① –FISHER L-100
② –MCB
①
②
°2θ
52
48
44
40
36
32
28
24
22

Table V, Crystal Form Composition of MCB & Fisher PbO_2

	% x-PbO_2*	% α-PbO_2	% β-PbO_2
MCB	81	1	18
Fisher	22	28	50

* This is a third crystalline form given in the x-ray table (15).

In addition to the apparent difference in surface areas which may affect the relative capacity for NO, it is obvious that the principal crystal forms of the samples also differ. It is well known that crystal form can measurably affect the reactivity of a compound. Therefore, an investigation of various PbO_2 synthesis routes with respect to the resulting crystal form of the product was conducted. The following equations depict the routes investigated:

$$2Pb(Ac)_2 + Ca(ClO)_2 + 4NaOH \xrightarrow{\Delta} 2PbO_2 + CaCl_2 + 4NaAc + H_2O \quad (a)$$

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O \quad (b)$$

$$Pb(Ac)_4 + 2H_2O \rightarrow PbO_2 + 4HAc \quad (c)$$

$$2PbO \overset{e^-}{\rightleftharpoons} PbO_2 + Pb \quad (d)$$

The PbO_2 from reactions (a) and (b) was only slightly crystalline and the PbO_2 from reaction (c) was almost totally noncrystalline (amorphous) as shown in Figure 2. None of the above showed any measurable reactivity toward NO. Reaction (d), the lead-acid battery plate formation reaction, yields a highly crystalline PbO_2 which has been characterized by Baker (16) and Bode (17). The electrolytically produced PbO_2 obtained from plate material of a lead-acid storage battery, after being HNO_3 washed, gave excellent recovery of NO as shown in Table I.

Figure 2

X-RAY DIFFRACTION SPECTRUM OF PbO_2 PRECIPITATED FROM $Pb(Ac)_4$

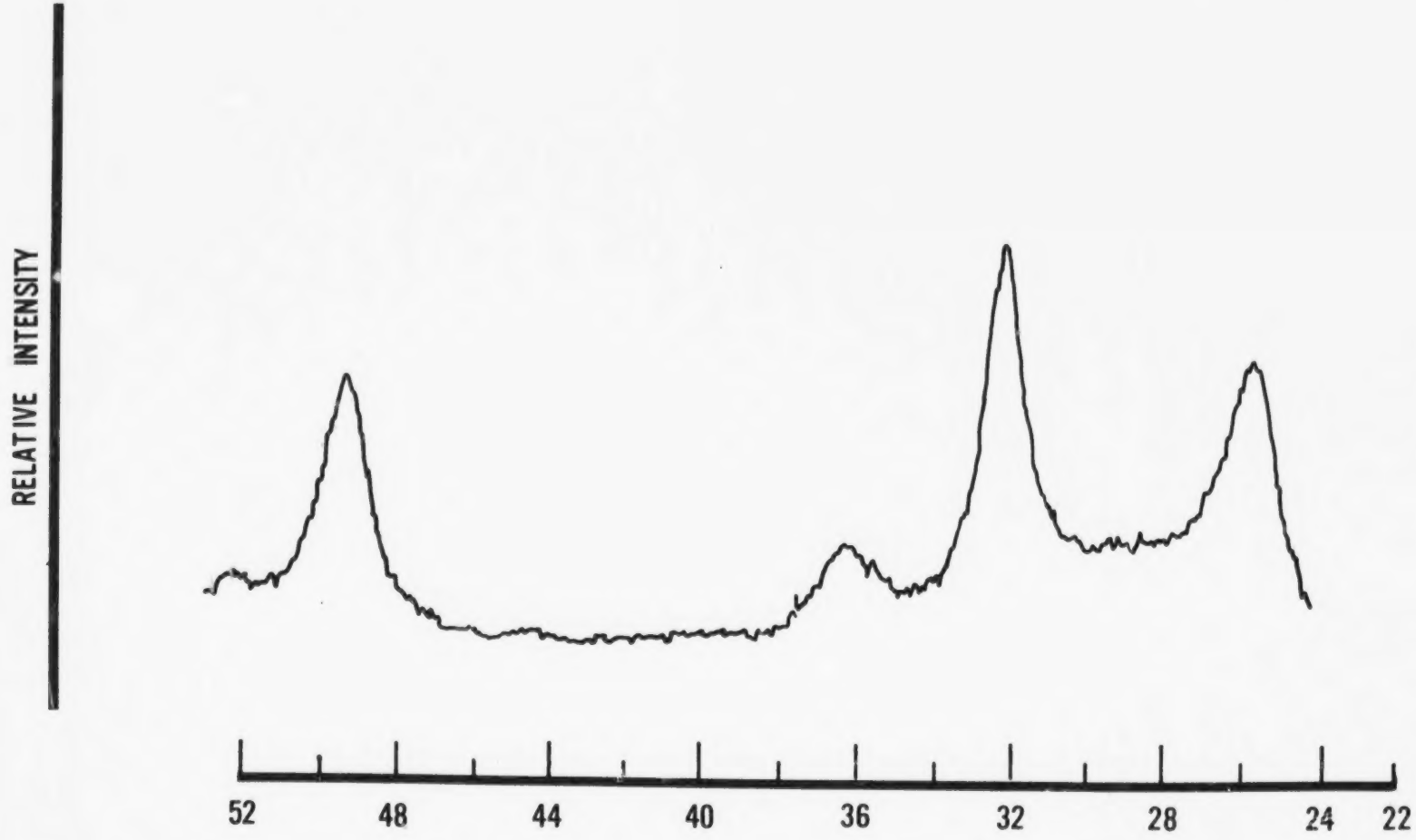


Table VI, Recovery From a 211 ppm NO/N_2 Source Using Electrolytically Produced PbO_2

Sample No.	ppm NO Recovered	
	Non-acid washed	Acid washed*
1	69	217
2	80	217
3	70	194
4	69	194
5	65	212
6	70	1[illegible]3
7	65	198
8	64	198
Average	69	205
% Recovered	33	97

* Prepared according to Pregl.

The low recovery illustrated by the non-acid washed PbO_2 data demonstrates the need to remove oxidizable material from the PbO_2 such as elemental lead which can lead to formation of reduced nitrogen species, i.e., $2Pb + 2NO \rightarrow 2PbO + N_2$.

Since Cropper (8) demonstrated that surface area plays a role in the NO_2 capacity of PbO_2 the MCB product was ball-milled for three days and retested with the 211 ppm NO/N_2 source. Table VII shows those results.

Table VII, Comparison of NO Recovery Using "As Received" and Ball-Milled MCB PbO_2

Sample No.	ppm NO Recovered	
	"As Received"	Ball-Milled
1	25	78
2	23	72
3	56	72
4	27	[illegible]
$\bar{X}$	33	75
% recovered	16	35

Apparently the source (crystallinity) of the PbO_2 is a more important factor than surface area. Further refinement of the PbO_2/SIE method using electrolytically derived PbO_2 is discussed in the following sections.

2.0 Analysis Methods

2.1 Laboratory Standard NO Sources.

The necessity for obtaining or preparing verified sources of NO for accomplishing Phase II of this program is recognized. Therefore a lecture bottle of Matheson "Analytical Reagent Grade" NO was analyzed on a CEC/DuPont 21-490 mass spectrometer. The only impurity found was less than 1% N_2, and no NO_2 was detected. An NO source in He was prepared using pressure measurements, which calculated as 256 ppm NO (v/v). This dilute source was verified by gas chromatographic (GC) analysis, after the GC was calibrated with the pure NO source using an exponential dilution flask. The average of seven determinations was 251 $\pm$ 6ppm NO for the GC method. The standard deviation (6ppm NO) for the GC analysis shows no significant difference between it and the calculated 256 ppm NO. Both a 1% NO/N_2 and a 1% NO_2/N_2 source were prepared (verified by mass spectrometer) from which a 200 ppm source of each was obtained by dilution. The 211 ppm NO/N_2 source was prepared in a large volume "K" bottle directly from the pure NO source by means of pressure measurements. The use of pressure measurements was shown to be sufficiently accurate for standard preparation. The large volume assured the use of a single source for the entire program.

2.2 Phenoldisulfonic Acid (PDS) Method Improvement

Initially, the published PDS method (3) was used for the determination of NO_3^- derived from flask samples of the verified NO laboratory source during the Phase II laboratory studies. It was necessary to first obtain a calibration curve using $NaNO_3$ standard solutions (250 µg/ml)

added to 20-25 ml of the 0.1 N sulfuric acid/H_2O_2 solution. The evaporation was accomplished in beakers as well as evaporating dishes, after carefully neutralizing the H_2SO_4.

A large random variability was noticed in the color intensity of the yellow nitro-PDS product, as well as undissolved silica turbidity from time to time. It was further noticed that when the acid H_2O_2 was excluded from the $NaNO_3$ standards an acceptable calibration curve was possible in the range from 1.0 to 5.0 µg NO_2/ml or 100 to 500 µg NO_2 per 100 ml vol. flask. When the turbidity was present low values were recorded even after the yellow solution was filtered prior to measurement in the 1 cm cell. During the initial analysis studies we were unable to obtain quantitative NO recovery when the 2 liter flask was filled with the known laboratory NO source. At this point it was decided to investigate the causes of the difficulties in an attempt to improve the precision and the accuracy of the PDS method.

2.2.1 Evaporation Step

A literature survey (10, 12-14) revealed that much work had been accomplished in investigating sources of errors in the PDS method for the determination of NO_3^- in potable water. Chamot, et al, (12-14) rarely mentioned encountering solids, or turbidity, following the nitration step, because only little NaOH is necessary for neutralization of potable water prior to the evaporation step. Thus, the etching (dissolution) of glass (silica) which produces turbidity was minimized. Therefore, as an initial step, it was decided to use 25 ml platinum (Pt) crucibles and only a 4 to 6 ml aliquot of the acidic H_2O_2 instead of evaporating the entire 25 ml as mandated (3).

The variability study, using this procedure, consisted of ten replicates each of four standard NO_3^- concentrations equivalent to 1, 2, 3 and 4 µg NO_2/ml. The standards were added to 3ml of a 0.1N H_2SO_4/3% H_2O_2 solution plus 1ml of 1N NaOH for neutralization. The evaporated residue was treated with 2ml of PDS and allowed to stand for 2 to 3 minutes prior to dilution. Some gas evolution was noted, but no turbidity was observed. Color intensity was measured at 405nm on a Cary Model 14 Spectrophotometer. The results are shown in Figures 3 and 4 and Table VIII:

Table VIII, Summary of PDS Variability Study

µg NO_2/ml (x)	av. absorbance @ 405nm ($\bar{y}$)	n	s
1	0.16	10	0.01
2	0.28	10	0.04
3	0.44	10	0.03
4	0.61	10	0.05

s = standard deviation

$\bar{y}$ = average absorbance

A regression equation was derived from the above data and was found to be $y = 0.15x-0.003$ where x = µg NO_2/ml. The slope of the calibration curve corresponds to about 0.15 absorbence per µg NO_2/ml if a 1 cm cell is used.

2.2.2 Neutral H_2O_2

The variability, however, was still not satisfactory; therefore, it was postulated that the gas evolution indicated earlier was not only CO_2 escaping but also HNO_3 from the anhydrous PDS solution. To test this hypothesis and to determine if a KOH instead of NH_4OH final

Figure 3

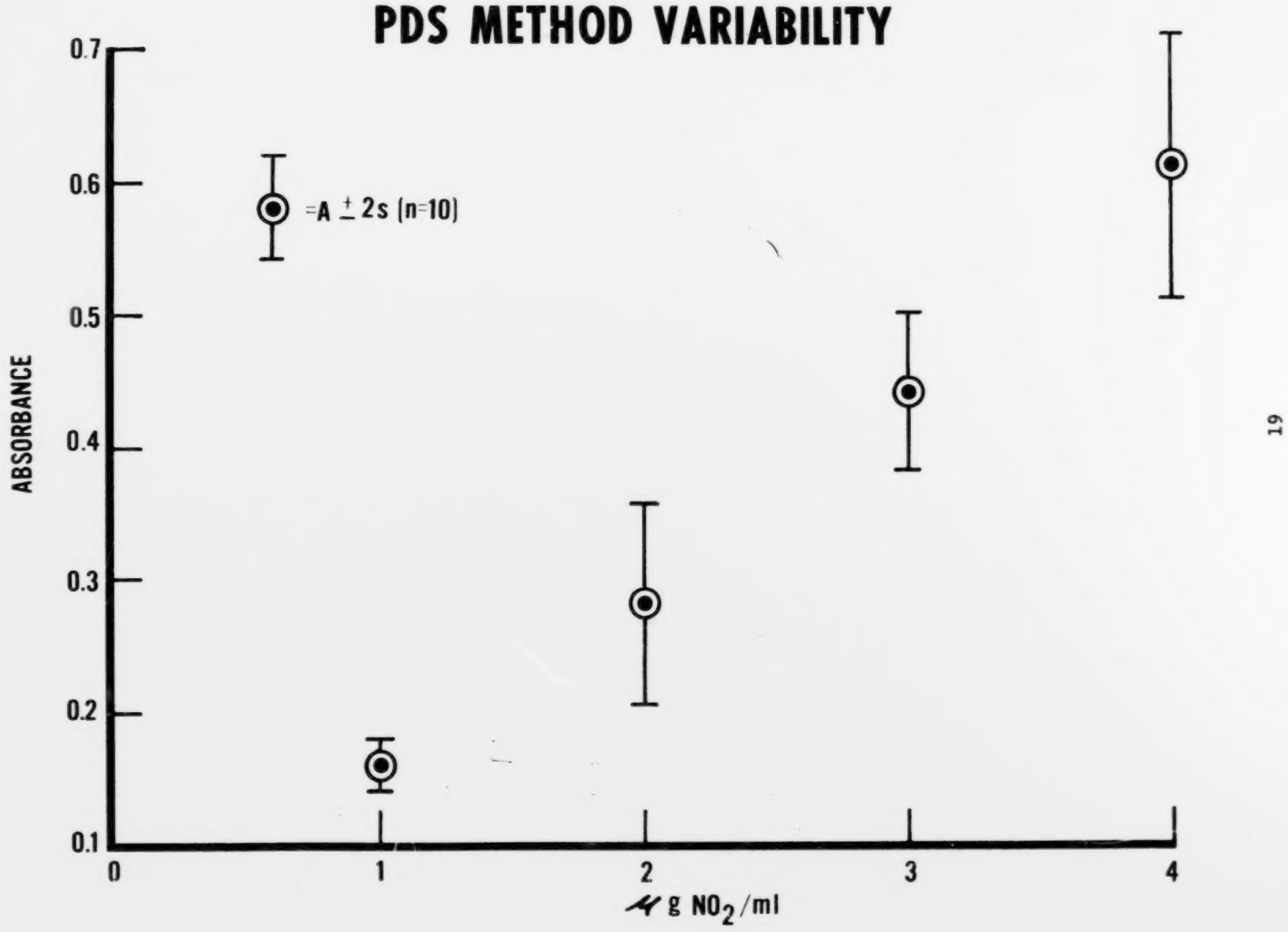
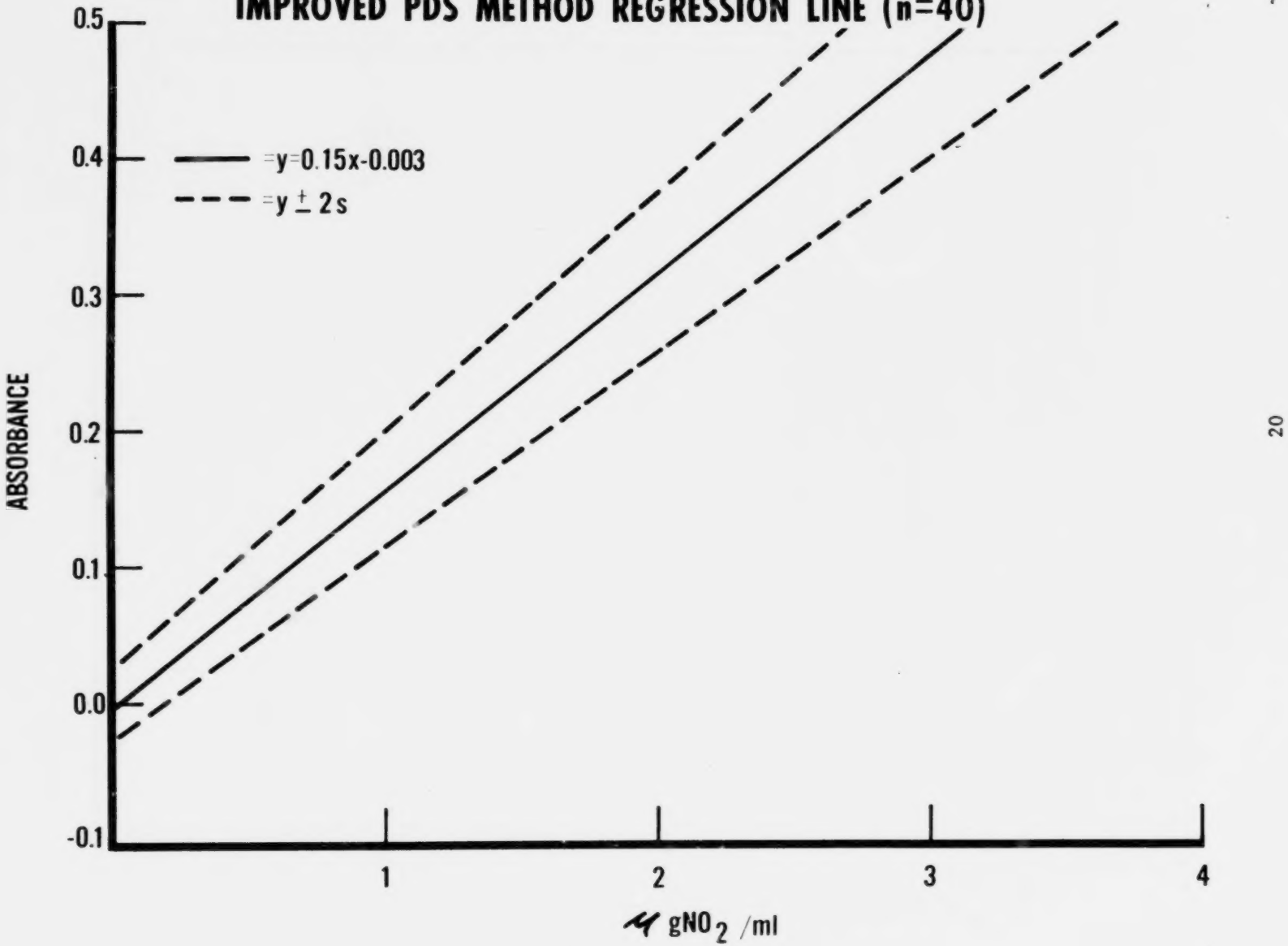

PDS METHOD VARIABILITY
ABSORBANCE
0.7
0.6
0.5
0.4
0.3
0.2
0.1
=A ± 2s (n=10)
0
1
2
3
4
μg NO2/ml

Figure 4


IMPROVED PDS METHOD REGRESSION LINE (n=40)
=y=0.15x-0.003
=y ± 2s
ABSORBANCE
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
1
2
3
4
gNO2 /ml

neutralization (12) yields a more intense color, neutral 3% H_2O_2 was substituted for the acidic peroxide, and both neutralization techniques were used. The results of this study using a concentration of 2.5µg NO_2/ml are summarized in Table IX.

Table IX, Comparison Between KOH and NH_4OH Neutralization (neutral 3% H_2O_2)

Parameter	KOH	NH_4OH
n	10	10
$\bar{y}$	0.40	0.38
s	0.007	0.005

$\bar{y}$ = av. absorbance @ 405 nm in a 1cm cell

s = std. deviation

n = number of replicates

It should be noted that there is no significant difference between the results of the two neutralization reagents. The precision is much better than that of Table VIII for similar concentrations. This increased precision confirms the Chamot, et al, (12) data that CO_2 evolution results in variability and loss of color.

2.2.3 NO Recovery

Using the modified PDS method, four two-liter flasks were prepared with 25ml of neutral 3% H_2O_2 and the verified 256 ppm NO/He source was sampled. After 16 hours, a 5 ml aliquot was taken from the flask and analyzed and followed by second aliquot taken for analysis a week later. A drop of 1N NaOH was added to each aliquot to assure that alkalinity was maintained during evaporation. The results of both

are given in Table X.

Table X, NO Recovery

Sample No.	ppm NO (v/v) after 16 hrs	ppm NO (v/v) after 1 wk
1	236	218
2	236	218
3	225	210
4	245	236
$\bar{X}$	235	221

$\bar{X}$ = average of each set.

It is apparent that some NO_3^- adsorption on glass occurs with standing. This was again observed when six flasks were filled with the 256 ppm NO/He standard and analyzed sequentially with time (hrs) in order to determine the absorption time for the NO by the neutral 3% H_2O_2. The results are shown graphically in Figure 5 and Table XI.

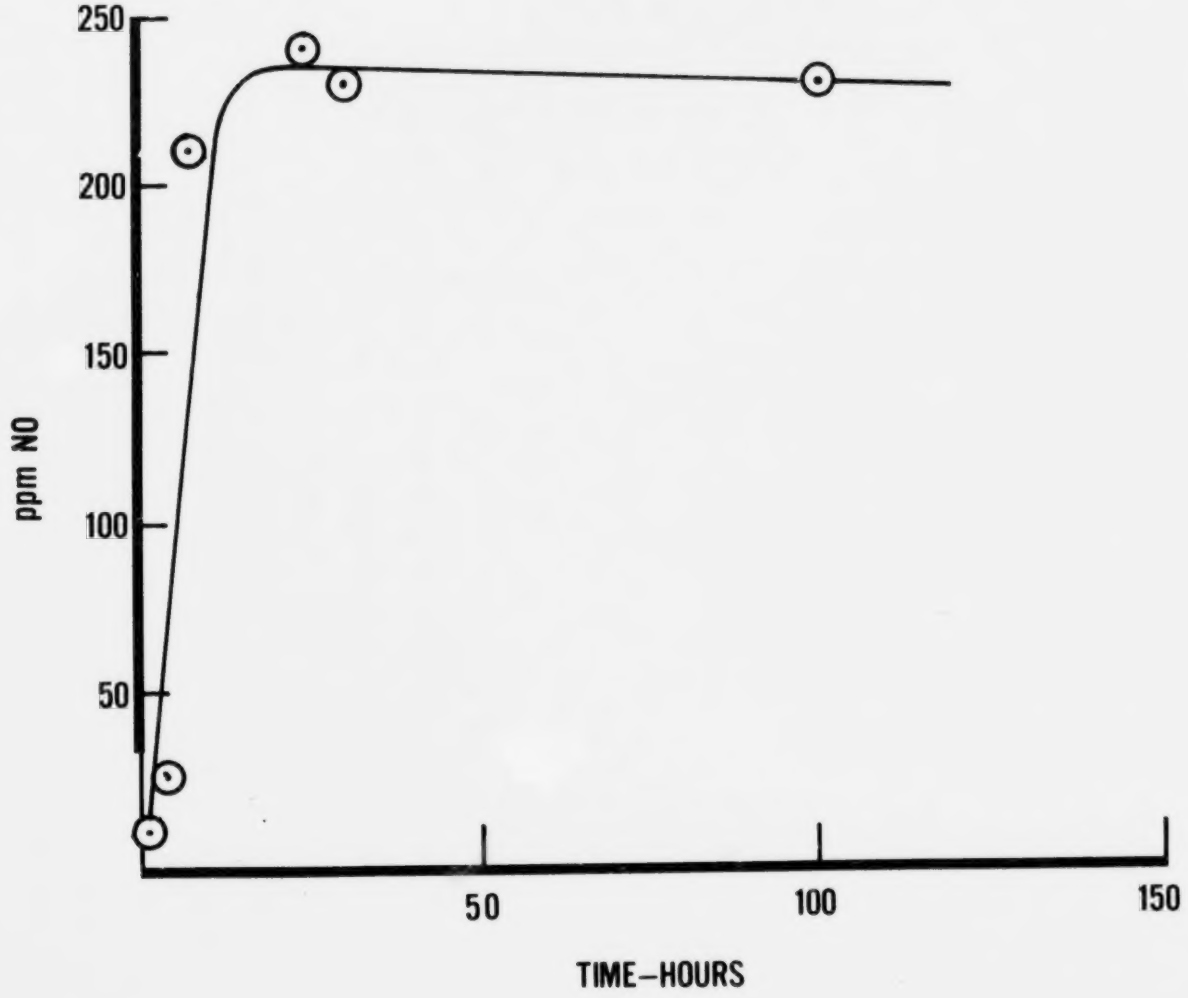
Table XI, NO Absorption vs Time

Time	ppm NO
1 hour	10
3 hours	31
7 hours	222
24 hours	240
30 hours	230
100 hours	230

It can be seen from Figure 5 and the above that the minimum of 16 hours standing, as required by Method 7, is necessary before opening the flask for the removal of a 5 ml aliquot. Conversely, maximum absorption of

Figure 5

NO ABSORPTION VS TIME (3% NEUTRAL H_2O_2)



NO_2 at the 200 ppm level was observed to take place in 3 hrs, see Figure 6. In a further experiment it was hoped to determine the lowest NO level for which the 2-liter flask could be effectively used. At low NO levels the initial reaction of NO and O_2 to give NO_2 in the vapor space of the flask may proceed slowly enough so that the 16 hour standing time is insufficient. Therefore, four replicates each of five concentrations of NO/N_2 over the range of 50 to 500 ppm NO (v/v) were admitted to evacuated flasks. The NO levels were determined as before and the results are shown graphically in Figure 7 and summarized in Table XII. It can be seen that the recovery decreases rapidly below 150 ppm NO if the flasks are allowed to stand only 16 hours.

Table XII, NO Recovery vs Concentration (16 Hours Standing Time)

ppm NO		
Calculated	Recovered	% Recovery
58	41	71
105	84	80
199	184	92
211	197	93
540	482	88

Several conclusions can be drawn from the preceding recovery data:

(a) the rate controlling step in conversion of gaseous NO to aqueous NO_3^- is the gas phase oxidation of NO to NO_2 and this oxidation rate is inversely proportional to the NO concentration.

(b) for samples which contain low concentrations (<150ppm) of NO, a compromise is necessary between sufficient NO oxidation time and NO_3^- losses in the glass flask,

Figure 6

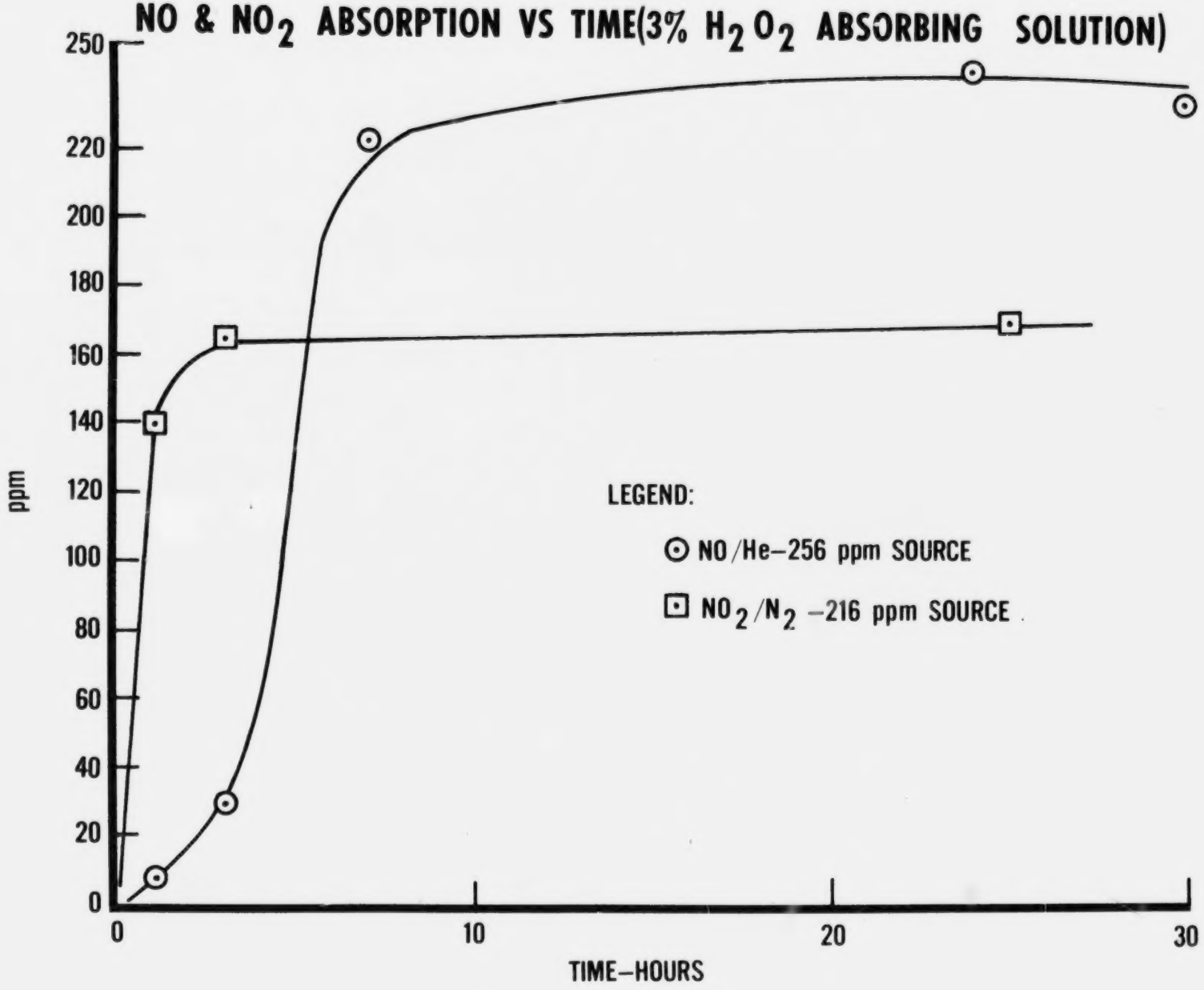
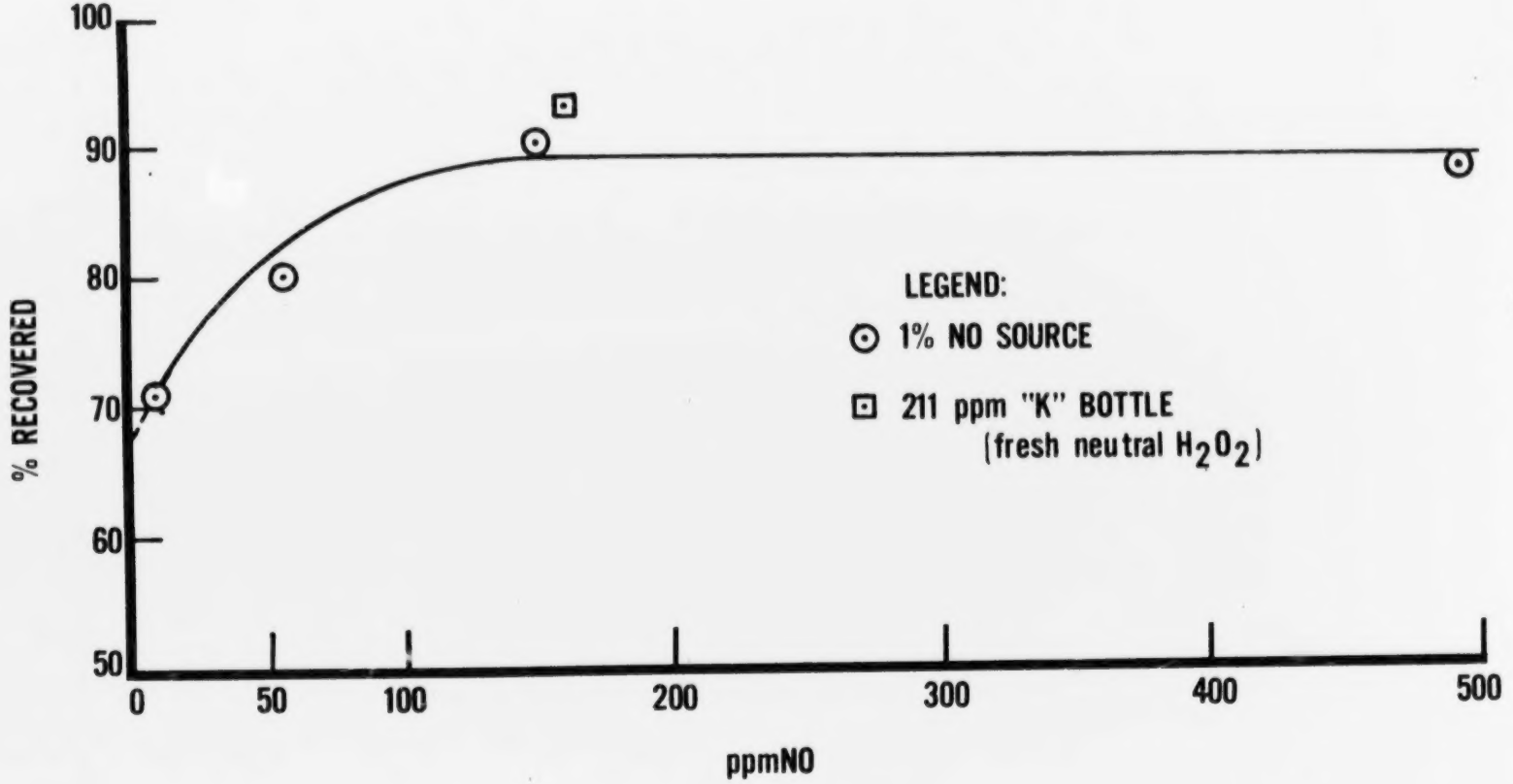

NO & NO2 ABSORPTION VS TIME(3% H2O2 ABSORBING SOLUTION)
250
220
200
180
160
140
120
100
80
60
40
20
0
ppm
0
10
20
30
TIME–HOURS
LEGEND:
NO/He–256 ppm SOURCE
NO2/N2 –216 ppm SOURCE

Figure 7

NO % RECOVERY VS NO CONCENTRATION(3% NEUTRAL H_2O_2)



(c) a larger flask will likely not reduce the NO losses at low levels because of the diffusion controlled gas phase and absorption reactions.

2.2.4 PbO_2 Nitrate Analysis by PDS

At about the time that improvements in the accuracy and precision of the PDS method were accomplished and incorporated into a "Suggested Amendment" to Method 7 (3), the PbO_2 sampling "variability" problems had also been solved (see Section 1.3). Thus it seemed desirable from a statistical point of view to be able to determine the NO_3^- content of the centrifuged aqueous solution obtained from the PbO_2 tubes by both SIE and PDS.

The ten PbO_2 tube samples obtained during the Hercules Field Test No. 1 (see Section 4) presented the first opportunity for obtaining such comparative data. The Table XIII results, shown below, indicate that the methods agree within 10% most of the time.

Table XIII, Comparative NO_x Results

Sample #	ppm NO_x (v/v) SIE	PDS
1-1	450	570
1-2	640	620
1-3	660	600
2-1	560	550
2-2	620	580
2-3	590	620
2-4	890	910
2-5	640	690
2-6	530	580
2-7	540	580

The data also revealed several problem areas which may account for the observed random differences. A pH dependence (see section 2.3.3) was observed to be responsible for poor precision in the PbO_2/SIE results. This was corrected by adding a phosphate (PO_4^{3-}) buffer to the extract, thus stabilizing the pH at about 11. Five replicates of the 211 ppm NO/N_2 source using PbO_2 tubes were analyzed for NO by both SIE and PDS. The results shown in Table XIV indicate an improved precision.

Table XIV, Comparison Between SIE and PDS with 211 ppm NO/N_2 Source

Test #	ppm NO (v/v)	
	SIE	PDS
1	216	215
2	204	201
3	206	208
4	204	191
5	208	---

The results averaged 208 and 204 ppm NO for the SIE and the PDS methods. At this point it must be emphasized that the acceptable accuracy and precision of the two analysis methods are "tailored" for stationary sources from which other reactive gases are absent. These would be HCl, HF, CO and SO_2, all of which are assumed to react at 180°C with the highly active PbO_2 (see section 5.1). A more comprehensive development program was undertaken which will be described in Section 3.0.

2.3 The NO_3^- Selective Ion Electrode (SIE)

2.3.1 Description

The usual determination of trace NO_3^- (10^{-4} to 10^{-6} M) in aqueous solutions has been accomplished for many years by colorimetry, of which the PDS method is only one example. Other techniques such as polarography have been used more recently. Since the advent of selective ion electrodes (SIE) an acceptably accurate result can be obtained in minimum time and by any operator. As with other methods, some knowledge of other ions present is necessary in order to minimize their interference. This aspect and the operation of such an electrode system is reviewed by Durst (18). The SIE data contained herein was obtained with

an Orion liquid membrane nitrate electrode, a Model 801 "Ionalyzer", and a Model 605 electrode switching unit. A Ag/AgCl reference electrode was used to develop the ΔV in mv. With the Model 605 electrode switch it is possible to obtain the NO_3^-, Cl^-, and F^- concentrations, if desired, as well as the pH of a sample with time savings and convenience. While the NO_3^- SIE has a limited lifetime, the restoration is relatively simple, and consists of replacing the membrane and the internal filling solutions.

2.3.2 Evaluation

The electrode system was calibrated seven times in eight days with standard solutions of $NaNO_3$. This should show what variability might be expected when the 100 ppm NO_3^- response is held constant. This calibration is necessary in order to define that range of concentrations where the least error occurs. Table XV shows the results and it appears that the range from 50 ppm NO_3^- to 500 ppm NO_3^- is most useful.

Table XV, Calibration of the Orion Liquid Membrane Nitrate Electrode

NO_3^- CONC	Electrode Response (mv.)						
(ppm)	15 Nov	16 Nov	16 Nov	17 Nov	17 Nov	19 Nov	22 Nov
10	197.3	198.0	202.5	197.6	197.6	191.2	192.5
20	180.0	180.5	177.1	180.8	178.6	177.3	176.5
50	151.0	152.5	149.7	146.5	156.8	153.2	142.6
100*	130.1	130.1	130.1	129.9	130.0	130.0	130.1
500	85.1	84.0	85.9	82.8	84.5	87.2	82.6
1000	62.7	63.0	63.1	66.2	62.9	65.5	60.5
10,000	7.5	5.0	3.0	5.5	4.6	7.0	-4.5

*100 ppm NO_3^- electrode response adjusted to 130.0 ± 0.1 mv prior to each run.

A linear regression analysis was performed on the electrode response data in order to determine the calibration curve and also to obtain an indication of the precision of calibration. Since the electrode response varies logarithmically with respect to the NO_3^- concentration, the log of the NO_3^- concentration was used for the regression analysis.

Results of Least Squares Analysis of NO_3^- Electrode Data

a. Best fit line is:

$y = -1.536 + 4.101$

where:

$y = \log_{10}$ (NO_3^- conc. (ppm))

and

x = electrode response (mV/100)

b. Standard error in y.,

$S_{\bar{y}} = 0.0515 = 1.1$ ppm NO_3^-

c. Standard error of intercept,

$(x = 0) = 0.0153 = 1.0$ ppm NO_3^-

All laboratory SIE data through the first (preliminary) Hercules nitric acid plant field test were obtained with the calibration techniques described. Some variation due to ambient temperature fluctuation was noted, since the electrode is subject to the Nernst equation which contains a temperature term:

$$E_{mv} = K + \frac{2.3RT}{ZF} \log a$$

where a = activity

K = constant

Z = ionic charge

and $\frac{RT}{F} = 59.16$ mv for singly charged ions at 25°C.

2.3.3 Sources of Error

As was mentioned in Section 2.2 the first Hercules results (Section 4.0) indicated some unexplained drifting in the electrode response. Some drift was observed even when $Pb(NO_3)_2$ standards were used for calibration (they more closely resemble the aqueous composition of the samples). The somewhat erratic results when compared with the PDS analysis of the same samples were thought to be due to this drifting response. In order to obtain better correlation between the two methods, another NO_3^- calibration curve was prepared using conditions which more nearly duplicate the actual sample. PbO_2 was added to each $Pb(NO_3)_2$ standard solution (10 ml $Pb(NO_3)_2$ solution/3 g PbO_2). These mixtures

were treated in exactly the same manner as an actual sample and a calibration curve was prepared. These solutions gave rise to a large signal drift similar to that encountered initially with the Hercules samples. A series of analyses of the 211 ppm NO/N_2 source using the PbO_2 sampling technique and this SIE calibration technique gave results which averaged 165 ppm NO. Grab samples and PDS analyses of the same source gave an average analysis of 205 ppm.

These results indicated that further refinement of the PbO_2/SIE system was necessary. A brief study showed that the SIE is pH sensitive to the extent of 5 mv per pH unit in the range pH 3-6. A study of the pH of several solutions encountered during the analyses gave the following results:

Table XVI, pH of Various Solutions Used During the PbO_2/SIE Analysis

Solution	pH
distilled H_2O + $NaNO_3$	6.5
distilled H_2O + $Pb(NO_3)_2$	5
distilled H_2O used to rinse PbO_2	3.2

It can be seen from Table XVI that the $NaNO_3$ solution is slightly greater than pH 6. The $Pb(NO_3)_2$ solution is less than pH 6 and within the pH dependent region. The distilled H_2O used to rinse PbO_2 was even more acidic. The literature revealed that H_2O and PbO_2 will react to a small extent as shown:

$$PbO_2 + H_2O \rightarrow H^+ + HPbO_3^-$$

It became apparent that some means to control the pH of the solution prior to the SIE measurement would be required. A 1000 ppm PO_4^{3-} buffer solution added to the $Pb(NO_3)_2$ standard solutions and to the

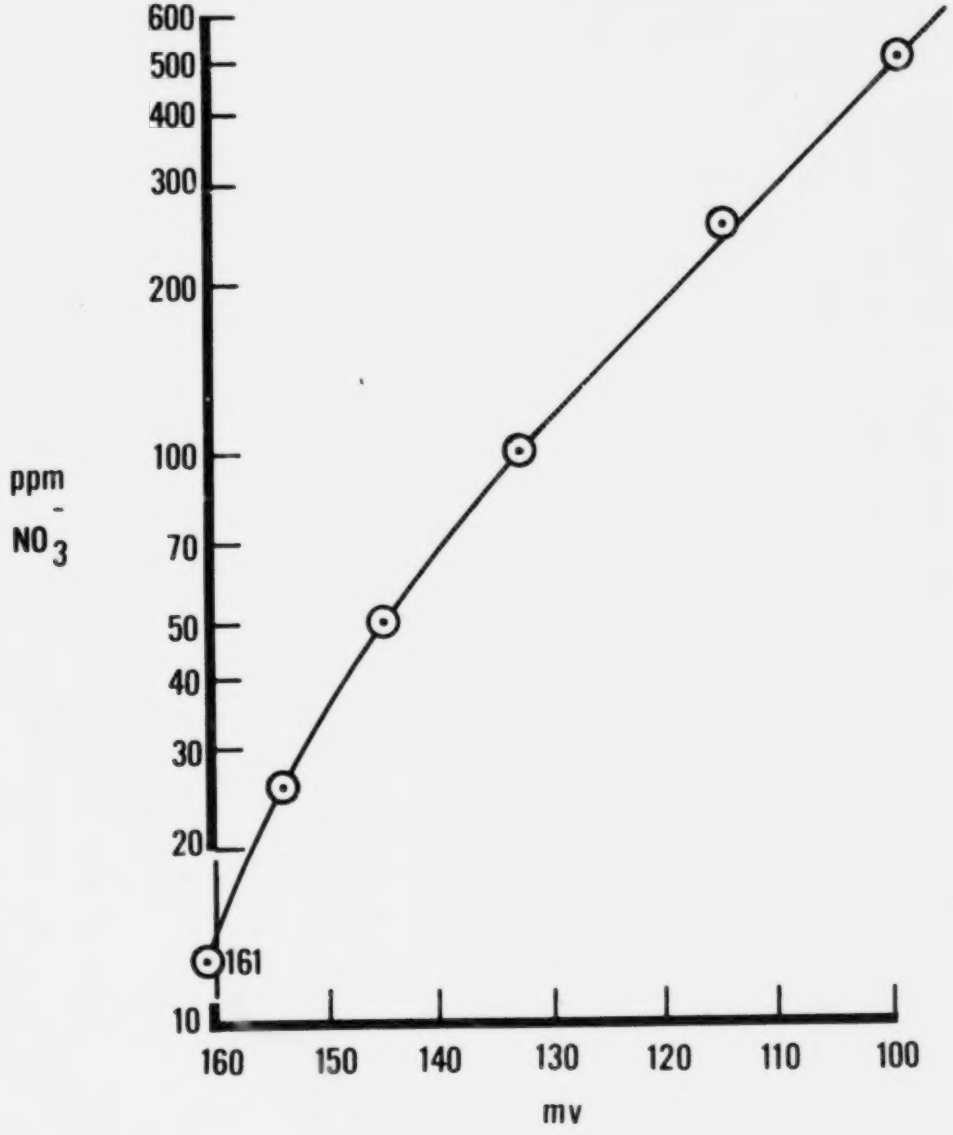
PbO_2 for NO_3^- extraction was sufficient to give a pH of 11 and also solved the drift problem that was initially encountered with the Hercules samples. The HPO_4^{2-} ion formed, reportedly constitutes a minimal interference to NO_3^- determinations (18). Figure 8 is a typical calibration curve using $Pb(NO_3)_2$ standards which were prepared in 1000 ppm PO_4^{3-} buffer. The addition of PO_4^{3-} apparently has no deleterious effect on the SIE calibration.

2.4 Final Analysis Methods Development

The PDS and SIE methods developed to this point have not been tested with simulated stack gas samples containing reactive or interfering gases such as HCl, HF, SO_2 and CO. Most of the later method changes were responses to deviations in results observed during the laboratory studies with HCl, HF, CO, and SO_2 in the presence of the NO stream. Details of the changes are described in Section 3.3 and Figure 9.

Figure 8

SIE CALIBRATION CURVE (1000ppm PO_4^{3-})



3.0 Laboratory Evaluation of Candidate Methods

3.1 NO recovery vs sampling rate. The 211 ppm NO/N_2 source was used throughout this series of tests and in all cases the $Pb(NO_3)_2$ was extracted at ambient temperature with 10.0 ml of 1000 ppm PO_4^{3-} buffer. Table XVII shows the analysis results using both the NO_3^- Selective Ion Electrode (SIE) and the Phenol Disulfonic Acid (PDS) methods.

TABLE XVII, Analysis Results From Sampling Rate Studies

Test No.	Flow Rate (ml/min)	Volume Sampled (l)	Ppm NO Found	
			SIE	PDS
1	18	17.8	191	---
2	41	2.85	212	---
3	68	3.94	199	214
4	135	3.58	204	196
5	253	3.80	216	204
6	256	3.84	223	202
7	513	4.10	212	190
8	513	4.10	203	196
		$\bar{X}$ =	208	200
		s =	10.2	8.3
		$\bar{X}$ - 211 =	-3	-11

All samples were collected at 190°C except test 3 which was collected at room temperature (~ 25°C). This result indicates that NO is quantitatively collected and oxidized to NO_3^- in the absence of gaseous O_2 even at room temperature. Test 1 represents an NO capacity test for the 4 mm I.D. tube

(2-4 g PbO_2) that was described in Section 2.3. The fact that the $Pb(NO_3)_2$ cannot be quickly extracted from the PbO_2 when large quantities of Pb^{2+} salts are present unless the PbO_2/extract slurry is heated for a short period of time may explain the slightly low result. This result does demonstrate that the capacity of the PbO_2 tube is much greater than the required amount of NO_3^- dictated by either analysis method.

3.2 NO recovery vs NO concentration. A 1.0% NO/N_2 mixture was used to prepare various NO/N_2 mixtures by dynamic flow dilution. The analysis results are presented in Table XVIII. Tests designated with "*" indicate that the sample was absorbed at ambient temperature instead of 190°C. Table XVIII illustrates that the PbO_2 sampling method can be expected to generally yield results that are accurate to within $\pm$ 5% of the actual NO value with either analysis method (SIE or PDS). The ambient temperature reactivity of electrolytically derived PbO_2 with NO greatly enhances its versatility as a sampling device. Almost any heating device can now be used because the tube needs only to be maintained at some temperature above the dew point of the sample gas.

3.3 NO recovery in the presence of other combustion products. Small flow rates of the pure combustion products (i.e., SO_2, HCl, ..., etc.) were diluted with the 211 ppm NO/N_2 source in a dynamic flow dilution system. This gas sample preparation method allows independent variation of the combustion product level without significantly affecting the NO concentration. Each combustion product was evaluated independently with the 211 ppm NO/N_2 source.

TABLE XVIII, Analysis Results From NO Concentration/Recovery Studies

Test No.	Ppm NO (theo.)	Volume Sampled (liters)	Ppm NO (Found)	
			SIE	PDS
1	64	10.49	51	55
2	64	10.54	60	65
3*	64	10.58	61	65
4	101	8.92	102	101
5	101	7.68	105	116
6*	101	10.08	104	96
7	211	4.37	203	228
8	211	4.31	210	220
9*	211	4.78	228	247
10	420	3.12	426	421
11	420	3.07	446	427
12*	420	3.21	428	409
13	664	2.42	633	656
14	664	2.32	624	673
15	664	2.37	609	624
16	900	1.44	880	897
17	900	1.66	863	891
18*	900	1.49	836	855

Linear regression analyses yielded the following data:

a. SIE: $x = 10.3 + 0.945y$; std error 19.1 ppm, std error of intercept 7.3 ppm, std error of slope 0.015

b. PDS: $x = 10.2 + 0.969y$; std error 16.6 ppm, std error of intercept 6.4 ppm, std error of slope 0.013

where x = theo and y = found

3.3.1 SO_2. Data contained in the Walden Research Corporation Report, Part 1, "Sulfur Oxides", demonstrate that SO_2 quantitatively reacts with PbO_2. Therefore, since $PbSO_4$ is an insoluble salt it seemed that SO_2 would not interfere with the NO reaction or analysis except through competition for oxidative sites on the PbO_2. Table XIX shows that this assumption was not valid and also demonstrates that NO can be determined in the presence of a ten-fold excess of SO_2. The PbO_2 was extracted with PO_4^{3-} buffer, centrifuged, and the supernatant liquid analyzed for NO_3^- in tests 1-3 of Table XIX. The data show an abnormal amount of scatter (PDS vs SIE) and indicate that something may be interfering with the SIE analysis. Since $Pb_3(PO_4)_2$ is much less soluble than $PbSO_4$ it is probable that the PO_4^{3-} contained in the aqueous extraction liquid is displacing the SO_4^{2-} in the $PbSO_4$ as follows:

$$3PbSO_4 + 2\ PO_4^{3-} \rightarrow Pb_3(PO_4)_2 + 3SO_4^{2-}$$

To test this hypothesis, cold water was used to extract the $Pb(NO_3)_2$ in tests 4a - 6a and the aqueous extract was decanted from the PbO_2 prior to adding sufficient buffer to make a final concentration of 1000 ppm PO_4^{3-}. The low results indicate that the $Pb(NO_3)_2$ either was not extracted quantitatively or had not been formed at the expected level. The PO_4^{3-} buffered extracts were returned to the appropriate PbO_2 samples, mixed, and allowed to stand overnight. These SIE results (tests 4b - 6b) are much too high, thus indicating a high degree of SO_4^{2-} interference. In further tests (7 - 9) the sample and aqueous extract volumes were decreased in view of the possibility that the PbO_2 capacity may have been exceeded.

TABLE XIX, NO Determination in the Presence of SO_2

Test No.	Treatment	Ppm NO/Ppm SO_2 (theo)	Volume Sampled (liters)	Ppm NO (Found)	
				SIE	PDS
1	PO_4^{3-}	211/1900	3.06	223	197
2	"	"	2.98	245	195
3	"	"	2.99	229	228
4a	Cold H_2O	211/2200	2.88	191	170
5a	"	"	3.13	187	169
6a	"	"	2.88	182	166
4b	PO_4^{3-}	"	----	277	---
5b	"	"	----	266	---
6b	"	"	----	275	---
7	Cold H_2O	"	1.94	192	186
8	"	"	1.94	184	174
9	"	"	2.02	183	195
10	Hot H_2O	211/2200	1.94	227	187
11	"	"	1.92	223	193
12	"	"	1.93	227	191
13	"	211/1080	1.94	211	211
14	"	"	1.92	211	217
15	"	"	1.93	222	217
16	Cold H_2O	"	2.12	204	222
17	"	"	2.41	193	216
18	"	"	2.06	195	216

No corresponding increase in the indicated NO concentration is apparent. Therefore, if the NO is being quantitatively trapped by PbO_2 it is then not being extracted completely by the water during the brief contact time (ca. 20 minutes). To increase the $Pb(NO_3)_2$ extraction rate, the PbO_2/water slurries were heated in boiling water with occasional shaking for 30 minutes in tests 10-15. These samples were then cooled in an ice bath and centrifuged prior to decanting the extracts. After adding

the appropriate amount of PO_4^{3-} buffer, the NO_3^- concentrations were determined. Acceptable results were obtained (ca. + 5% error probably due to SO_4^{2-} interference) thus demonstrating that the presence of SO_2 does not preclude accurate NO determination. To determine if the same extraction difficulty exists at the 5:1 excess SO_2 level, cool (25°C) water was again used to extract the NO_3^- and the SIE measurement was made after adding the appropriate amount of PO_4^{3-} (tests 16-18). The buffered extracts were then returned to the PbO_2 and the slurries were allowed to stand for 20 minutes after shaking. The corresponding PDS analysis results indicate that heating the aqueous extract is necessary even at the 5:1 excess SO_2 level, probably due to co-crystallization of $PbSO_4$ with $Pb(NO_3)_2$.

3.3.2 CO. Carbon monoxide was combined with the 211 ppm NO/N_2 source and the PbO_2 sampling method was used in conjunction with both the SIE and PDS analysis techniques. The analysis results are shown in Table XX.

TABLE XX, NO Determination in the Presence of CO

Test No.	Treatment	Ppm NO/Ppm CO (theo)	Volume Sampled (liters)	Ppm NO (Found)	
				SIE	PDS
1	Cold H_2O	211/3000	2.67	136	218
2	"	"	2.65	140	218
3	"	"	2.66	109	221
4	Hot H_2O	"	2.33	210	222
5	"	"	1.94	218	224
6	"	"	1.97	222	220

In tests 1-3, cold water was used to extract the PbO_2 and the extract decanted. The SIE measurements were made after the appropriate amount of PO_4^{3-} buffer was added. The corresponding PDS results were obtained after the buffered extracts were allowed to stand for 16 hours in contact with the PbO_2. The low SIE results indicate that CO also reacts with PbO_2 to form a slightly soluble co-crystal with $Pb(NO_3)_2$, (i.e., $PbCO_3 \cdot Pb(NO_3)_2$. Since $Pb_3(PO_4)_2$ is much less soluble than $PbCO_3$, the PO_4^{3-} releases the CO_3^{2-} and NO_3^- by displacement precipitation as evidenced by the corresponding PDS results. In further tests (4-6), the aqueous slurry was heated as in the SO_2 study for about 30 minutes followed by cooling the mixture in an ice bath prior to separating the extract. SIE and PDS measurements were made after the appropriate amount of PO_4^{3-} buffer was added to the separated extracts, and quantitative NO recovery is again indicated. Thus far, SO_2 and CO interference can be eliminated simply by heating the aqueous PbO_2 slurry.

3.3.3 HCl. Gaseous hydrogen chloride was combined with the 211 ppm NO/N_2 source in the dynamic flow dilution apparatus and Table XXI shows the SIE and PDS analysis results of the PbO_2 samples.

TABLE XXI, NO Determination in the Presence of HCl

Test No.	Treatment	Ppm NO/Ppm HCl(theo)	Volume Sampled (liters)	Ppm NO (Found)	
				SIE	PDS
1	Hot H_2O	211/2400	1.97	258	---
2	"	"	1.97	274	---
3	"	"	1.95	274	---
4	"	"	1.94	256	215
5	"	"	1.95	266	200
6	"	"	1.93	248	172
7	Electrolysis	"	1.95	207	182
8	"	"	1.93	172	162
9	"	"	1.93	188	162
10	Hot H_2O/PbF_2	"	1.95	192	182
11	"	"	1.93	209	212
12	"	"	1.97	207	199
13	"	211/1500	2.45	218	190
14	"	"	2.47	216	196
15	"	"	2.54	211	187

SIE results obtained from tests 1 - 6 indicate that $PbCl_2$ is not sufficiently insoluble and therefore interferes with both the SIE and PDS analyses when the earlier hot water extraction technique is used. The PDS results corresponding to tests 4 - 6 were obtained after Ag_2SO_4 was added to the extract. These results are also somewhat erratic, possibly due to absorption of NO_3^- by the AgCl and Ag_3PO_4 which was formed. An attempt to electrolytically strip the Cl^- from the extract with a silver billet electrode was made in tests 7 - 9. Low results from both the SIE and PDS

analyses indicate that NO_3^- was either absorbed by the AgCl, electrolytically reduced at the cathode, or evaporated as HNO_3 from the acidic solution (necessary for electrolysis). The complex salt, PbClF, has been used for many years for the gravimetric determination of Pb^{2+}, Cl^-, or F^-. The solubility of PbClF is somewhat lower than PbF_2 and F^- interferes with the SIE to the same degree as SO_4^{-2}. Therefore, the addition of excess PbF_2 to the PbO_2/water slurry prior to heating the mixture should result in the precipitation of PbClF as follows:

$$PbCl_2 + PbF_2 \rightarrow 2\ PbClF$$

The results of tests 10 - 15 indicate that the assumption is valid and acceptable NO recovery is indicated. Thus, chloride interference is eliminated through selective precipitation of PbClF.

3.3.4 HF. Gaseous hydrogen fluoride was combined with the 211 ppm NO/N_2 source in the dynamic flow dilution apparatus. The HF content of the gas mixture was calculated based on the assumption that only the monomer (HF) was present. However, it is well known that hydrogen fluoride can exist in various molecular multiples up to H_4F_4 in the gaseous state. Therefore, the HF level indicated in Table XXII may be conservative.

TABLE XXII, NO Determination in the Presence of HF

Test No.	Treatment	Ppm NO/Ppm HF (theo)	Volume Sampled (liters)	Ppm NO (Found) SIE	Ppm NO (Found) PDS*
1	Hot H_2O	211/1700	2.44	201	232
2	"	"	2.46	203	234
3	"	"	4.54	197	224
4	"	"	2.46	199	244

* Calibration standards did not contain F^- which may account for the +10% bias.

The hot water extraction method was used in tests 1 - 4 and acceptable recovery of NO is indicated for the SIE analysis method.

3.3.5 CO_2. Carbon dioxide was combined with the 211 ppm NO/N_2 source in the dynamic flow dilution apparatus and the SIE/PDS analysis results from PbO_2 samples are reported in Table XXIII.

TABLE XXIII, NO Determination in the Presence of CO_2

Test No.	Ppm NO/Ppm CO_2 (theo)	Volume Sampled (l)	Ppm NO (Found) SIE	Ppm NO (Found) PDS
1	211/14,000	2.53	219	222
2	"	2.94	215	218
3	"	2.79	214	201

Instead of extracting the $Pb(NO_3)_2$ with hot water as before, the 1000 ppm PO_4^{3-} buffer was added directly to the PbO_2 and the slurry was shaken for only two minutes prior to centrifuging and decanting the extract. If CO_2 reacts with PbO_2 a large error would be evident. The acceptable results verify that CO_2 did not react with the PbO_2.

3.4 Analysis of results. In the foregoing sections it has been demonstrated that the PbO_2 sample tube will quantitatively collect NO at flow rates of 20 to 500 cc/min, at NO levels from 50 to 900 ppm, and at reactor temperatures from 25°C to 190°C. In addition, it was also demonstrated that accurate NO analysis results can be obtained even in the presence of tenfold excesses of SO_2, HCl, CO, HF, and CO_2 by using a single sample preparation method and either of two analysis methods. Table XXIV describes the overall scatter obtained from those results of section 3.3 where the sample preparation techniques demonstrated that quantitative recovery occurred and interfering anions were eliminated through selective precipitation. In short, all PbO_2 tube samples known to be contaminated with SO_4^{2-}, CO_3^{2-}, Cl^- and F^- can be extracted with hot water containing excess PbF_2, cooled to 0°C, centrifuged, and the extract decanted prior to adding PO_4^{3-} buffer. This sample preparation technique minimizes the effects of interfering combustion products and allows accurate NO analyses.

TABLE XXIV, NO Recovery After minimizing the Effects of Interfering Combustion Products

Test No.	Interfering Combustion Product	Ppm NO Found (211 ppm theo)	
		SIE	PDS
10	SO_2	227	187
11	"	223	193
12	"	227	191
13	"	211	211
14	"	211	217
15	"	222	217
4	CO	210	222
5	"	218	224
6	"	222	220
10	HCl	192	182
11	"	209	212
12	"	207	199
13	"	218	190
14	"	216	196
15	"	211	187
1	HF/SiF_4	201	232
2	"	203	234
3	"	197	224
4	"	199	244
1	CO_2	219	222
2	"	215	218
3	"	214	201
	$\bar{X}$ =	212	210
	s =	9.6	17.5
	$\bar{X}$ - 211 =	+1	-1

4.0 Field Tests of Manual Methods

4.1 Field test experimental design. The field test program was designed in such a manner that the analysis error portion of the test could be isolated from the sampling error portion. This was accomplished by analyzing the tube and flask samples by both analytical methods (PDS and SIE). In addition, to compare sampling methods, two flask (grab) samples were taken concurrently with each tube (time-integrated) sample. The time period required to take each tube sample was divided into five segments and the two flask samples were randomly spaced within the five segment periods. Economics and space limitations dictated the number of flask samples to a maximum of thirty per field test. Therefore, each field test was divided into three equal sampling periods (3 days) during which five tube samples and ten concurrent flask samples were taken each period. The data matrix used is shown in Table XXV.

TABLE XXV, Data Matrix

		PbO_2	Tube	Sub Sample Order	2 Liter Flask I		II	
Day	Sample	SIE	PDS		SIE	PDS	SIE	PDS
1	1			3,5				
	2			1,2				
	3			1,5				
	4			3,5				
	5			1,2				
2	6			2,3				
	7			2,5				
	8			2,4				
	9			3,4				
	10			3,5				
3	11			3,5				
	12			1,2				
	13			1,3				
	14			2,4				
	15			2,3				

4.2 Field Test Analysis Scheme

The effects of other gases on the hot PbO_2 sampling tube (reactor) have been reported in section 3.3. Because some of these anions (Cl^-, F^-, SO_4^{-2}) will interfere with the SIE and/or PDS analysis methods, a special sample preparation procedure was developed for both the PbO_2 tube and flask grab samples. This procedure (Figure 9) was tested with aqueous $Pb(NO_3)_2$ and $NaNO_3$ standards for the SIE and PDS analysis methods respectively. In addition, triplicate tube and flask samples were taken using the 211 ppm NO/N_2 source, and each sample was analyzed by the SIE and PDS methods. This was necessary since the statistical data matrix (Table XXV) requires that the NO_x of each sample be determined by both analysis methods. Table XXVI shows the averages of three NO samples, ($3PbO_2$ tubes and 3 flasks) each analyzed by SIE and PDS.

TABLE XXVI, Ppm NO from 211 ppm NO/N_2 Source

Sampling Methods	Analysis Methods	
	SIE	PDS
Flask	257 ± 10	206 ± 2
PbO_2	204 ± 3	$221 \begin{smallmatrix} +13 \\ -23 \end{smallmatrix}$

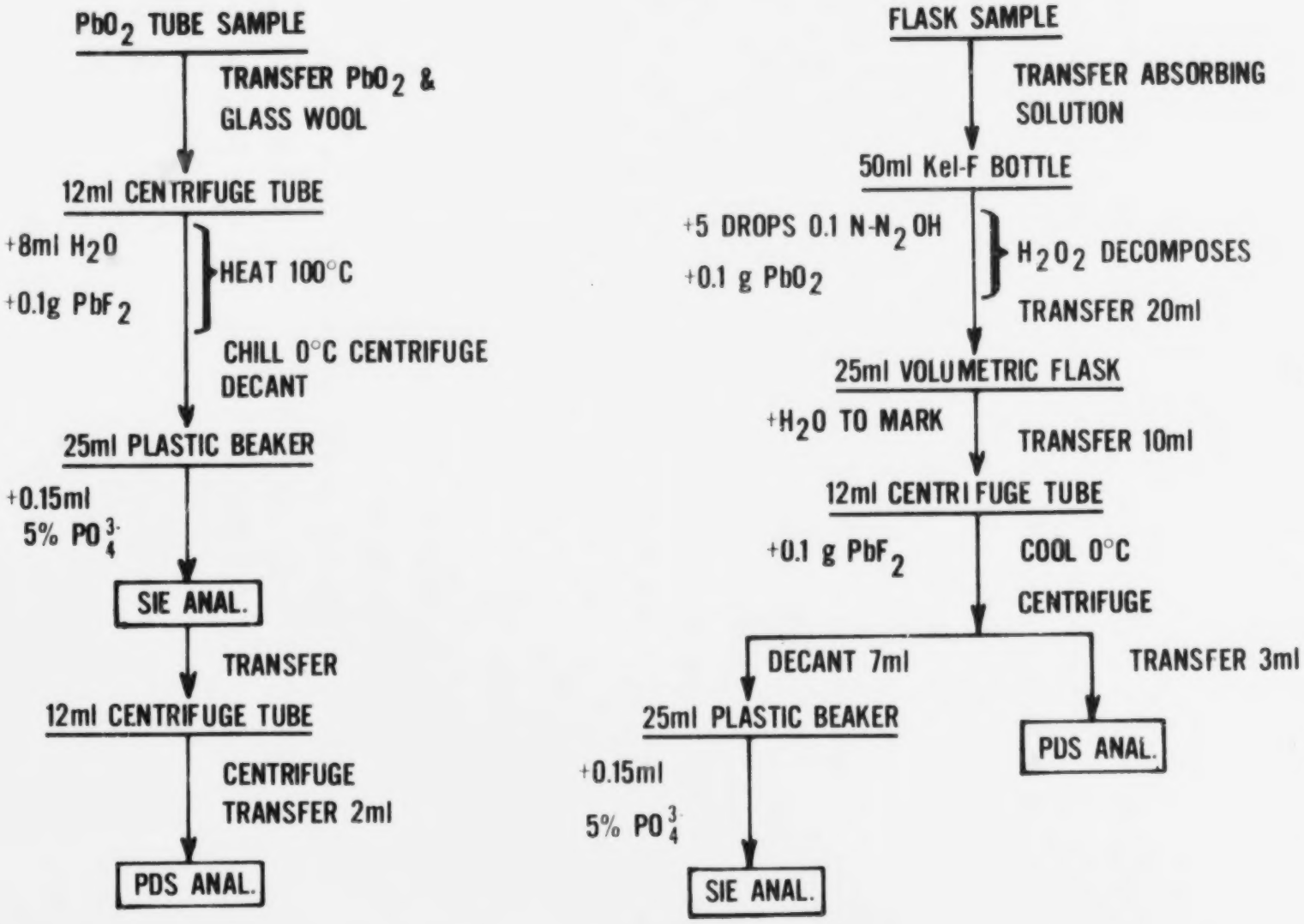
An analysis bias definitely exists for the flask-SIE and possibly for the tube-PDS combinations. However, the laboratory NO_x source does not contain the other anticipated stack gases for which the sample preparation procedure was developed. The Flask-SIE bias is likely introduced by the excessive amount of F^- which is released when the Na_3PO_4 buffer is added.

4.3 Field Test Data.

Sampling and analysis methods were identical for all of the

Figure 9

NO_x ANALYSIS SCHEME (FIELD TESTS)



field tests except Hercules Test No. 1. This test was conducted primarily to establish the reliability and sampling equipment requirements for a remote operation. The analysis methods used for this test are described in section 2.0. The sampling apparatus used for the remainder of the field tests is schematically represented by Figure 10. This apparatus was designed to allow flask and tube samples to be taken simultaneously from a common gas stream. The PbO_2 tubes (D) were maintained at 180°C. during the sampling process and the sample flow through each tube was metered to ∿ 100 cc/min by the valve at (G). The volume of gas sampled with each tube or flask (C) was determined by the following relationship:

$$V_g = \frac{P_f - P_o}{BP} V_b$$

where:

V_g = Volume of Sample

$P_f - P_o$ = Pressure change from A_1 or A_2

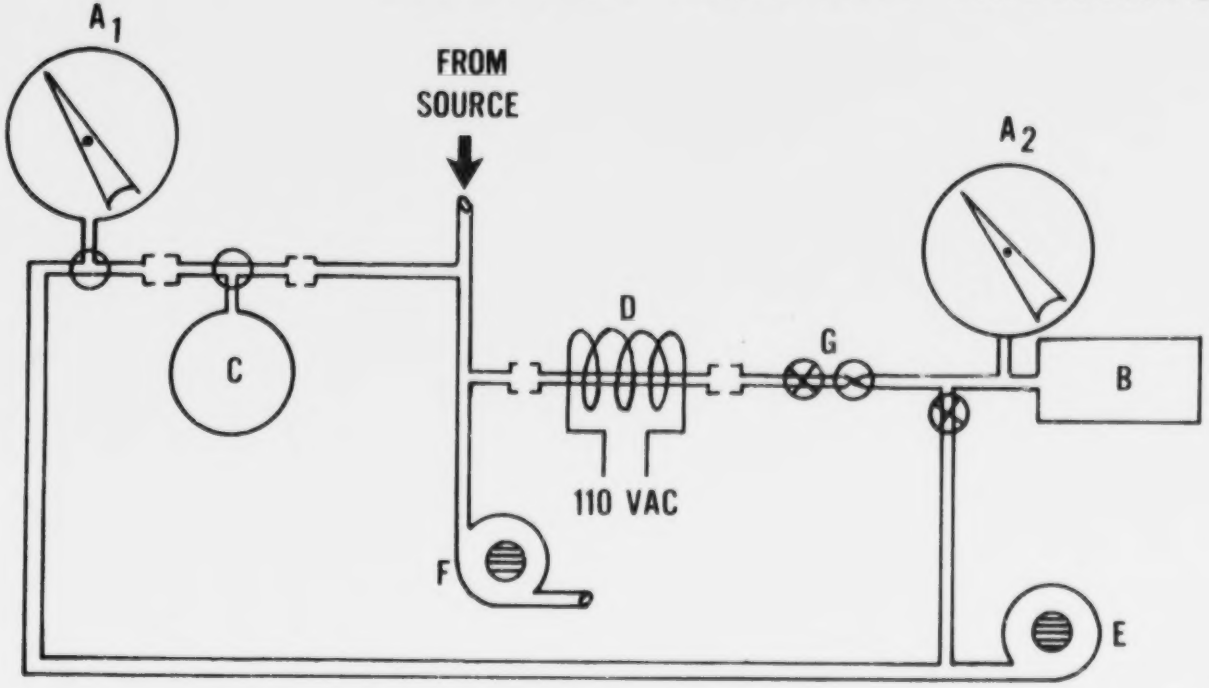
V_b = Volume of ballast or flask

BP = Barometric pressure

The size of the ballast (5 liters) was chosen so that an adequate sample could be collected for analysis without allowing the final sample pressure (P_f) to become high enough to condense the moisture in the combustion gas. For sources containing > 300 ppm NO_x, 1 liter of gas is sufficient for either the SIE or PDS method. This sampling technique was chosen because it is independent of flow rate changes through the tube and moisture condensation can be eliminated thus precluding a separate moisture determination for accurate emission level calculation.

Figure 10

FIELD TEST SAMPLING APPARATUS



LEGEND:

A1,A2 = 0-760mm ABSOLUTE PRESSURE GAUGE

B = 5 L. BALLAST VOLUME

C = 2 L. FLASK

D = PbO_2 TUBE WITH TUBE OVEN

E = VACUUM PUMP

F = AIR PUMP

G = TOGGLE & METERING VALVES

4.3.1 Hercules HNO_3 Plant. This plant uses the ammonia oxidation process for synthesis of N_2O_4 and HNO_3. The exhausted gas is saturated with H_2O at ~ 110°F and contains both NO and NO_2 in about equal concentrations. Although the plant operates on a continuous basis, the NO_x emission level varies rapidly over a wide range as shown by the raw data from the two field tests (Tables XXVII and XXVIII).

TABLE XXVII, Raw Data Hercules HNO_3 Plant

FIELD TEST NO. 1

1 February 72

TIME OF DAY	NO_x PPM/Vol		
	PDS(1)	SIE(2)	(PDS)
1300	600	---	
1315	560	---	
1335	650	---	
1350	630	---	
1410	570	---	
1500	---	450	(570)
1520	---	640	(620)
1545	---	660	(600)
2 February 72			
1005	500		
1020	640		
1040	720		
1100	---		
1117	550		
1215	---	560	(550)
1315	---	620	(580)
1340	---	590	(620)
1410	---	890	(910) *
1440	---	640	(690)
1510	---	530	(580)
1540	---	540	(580)
$\bar{X}$ =	602	581	(599)
s =	66	68	41

(1) Flask/PDS

(2) PbO_2 tube/SIE (PDS)

* Not included in $\bar{X}$ and s because plant changed operating parameters during sample period.

TABLE XXVIII, Raw Data, Hercules HNO_3 Plant

FIELD TEST NO. 2 (PPM NO_x)

		PbO_2	Tube	Sub Sample Order	2 Liter Flask			
					I		II	
Day	Sample	SIE	PDS		SIE	PDS	SIE	PDS
1	1	568	705	3,5	319	412	323	378
	2	565	605	1,2	398	517	314	410 *
	3	557	535	1,5	296	415 *	526	621
	4	491	506	3,5	468	532	386	437
	5	440	435	1,2	413	439	433	440
2	6	35 3	335	2,3	402	446	400	443
	7	365	346	2,5	345	385	368	428
	8	370	370	2,4	362	414	368	413
	9	472	514	3,4	486	551	509	567
	10	596	640	3,5	695	610	619	612
3	11	624	755	3,5	773	874	664	644
	12	575	660	1,2	713	723	761	776
	13	579	650	1,3	694	741	648	711
	14	542	587	2,4	625	647	630	563
	15	551	648	2,3	628	584	672	822
	$\bar{X}$	510	553				544	576
	s	90	132				142	141

* Samples above the line leaked air and are not included in statistics

Paired "t" results (95% level):

tube/SIE ≠ tube/PDS ≠ Flask/PDS

An extended grab sample technique was used with the 2 liter flask samples during Test No. 1 and all tube samples were analyzed by both the PDS and SIE methods. The use of the extended grab sample technique with this variable source may account for the significantly better agreement between the tube and flask samples when compared to the tube and flask data from Test No. 2.

4.3.2 Moapa Power Plant. The Nevada Power Company coal-fired power plant at Moapa, Nevada, uses a low sulfur type of coal. The SO_x level of the flue gas is reportedly about 300 ppm. The source variability was much less than that of the Hercules HNO_3 plant as shown in Table XXIX. The significantly higher values for the flask samples are due to an undetermined amount of moisture condensation in the flasks.

4.3.3 Gas Fired Boiler. The third source sampled was a natural gas fired boiler which is rated in excess of 150 h.p. Samples were taken from a probe located directly above the heat exchanger tubes. The gas temperature at this point is normally about 400°F. However, since the field test was conducted in the summer, the boiler was not operating at full capacity as evidenced by the low NO_x level indicated by Table XXX. Only the PbO_2 tube data is shown because the 2 liter flasks contained too little sample for analysis. The gas volume passed through each tube was approximately 4 liters in order to obtain a large enough sample for analysis. The ability to vary the sample size commensurate with the NO_x emission level represents a marked improvement, among others, over the simple grab sample technique.

TABLE XXIX, Raw Data, Moapa Power Plant

Field Test (ppm NO_x)

			PbO_2 Tube		Sub Sample	2 Liter Flask I		II	
Day	Sample		SIE	PDS	Order	SIE	PDS	SIE	PDS
1	1		619	688	3,5	676	691	654	650
	2		620	582	1,2	674	734	651	711
	3		622	615	1,5	665	679	674	625
	4		621	686	3,5	683	639	666	764
	5		615	661	1,2	646	817	664	730
2	6		598	566	2,3	692	682	691	635
	7		589	586	2,5	693	575	663	688
	8		569	616	2,4	650	535	632	587
	9		550	570	3,4	652	573	643	617
	10		561	535	3,5	675	606	635	580
3	11		530	524	3,5	640	628	619	518
	12		538	474	1,2	593	526	594	610
	13		539	467	1,3	549	519	592	619
	14		537	492	2,4	567	576	554	498
	15		527	500	2,3	564	530	596	499
		$\bar{X}$	576	571				638	621
		s	38	73				43	82

Paired "t" results (95% level):

tube/SIE = tube/PDS ≠ Flask/PDS

TABLE XXX, Raw Data Gas Fired Boiler Field Test

Day	Test	Ppm NO_x (tube)	
		SIE	PDS
1	1	17	18
	2	16	17
	3	15	16
	4	18	17
	5	15	17
2	6	17	23
	7	15	23
	8	13	20
	9	3	7
	10	15	19
3	11	19	28
	12	19	26
	13	15	18
	14	17	24
	15	16	18
	$\bar{X}$ =	16	20
	s =	1.7	3.8

This field test clearly illustrates that the PbO_2 tube time-integrated sampling method is much more versatile than the grab sampling technique which is strictly limited to higher NO_x levels.

4.3.4 Diesel Auxiliary Power Generator. The final stationary source tested was the exhaust of a large six-cylinder diesel powered electric generator. This test was unique with respect to potential interferences. The engine was operated under load but with an extremely fuel-rich mixture ratio as evidenced by a noticeable amount of unburned fuel

which condensed on the inside walls of the 2 liter flasks. The NO_x level appeared to be very constant and apparently moisture condensation in the flasks did not significantly affect the results. This data is shown in Table XXXI. It should be noted that the unburned hydrocarbon mist did not interfere with the PbO_2 collection of NO.

TABLE XXXI, Raw Data From Diesel Aux. Power Generator (ppm NO_x)

		PbO_2	Tube	Sub Sample Order	2 Liter Flask I		2 Liter Flask II	
Day	Sample	SIE	PDS		SIE	PDS	SIE	PDS
1	1	411	365	3,5	444	353	422	318
	2	354	277	1,2	443	454	487	353
	3	384	291	1,5	501	398	438	382
	4	391	289	3,5	446	364	459	339
	5	390	301	1,2	479	411	451	346
2	6	330	324	2,3	383	385	383	298
	7	337	298	2,3	361	350	383	349
	8	366	299	2,4	386	350	416	363
	9	363	299	3,4	406	332	433	341
	10	372	302	3,5	398	339	420	349
3	11	406	343	3,5	460	424	461	367
	12	377	502	1,2	494	403	489	431
	13	361	379	1,3	466	362	439	416
	14	362	372	2,4	446	355	457	372
	15	375	364	2,3	453	373	449	369
	$\bar{X}$ =	372	335				438	368
	s =	23	58				36	21

Paired "t" results (95% level):

tube/SIE = flask/PDS ≠ tube/PDS

4.4 The Field Test Data is summarized in Table XXXII.

TABLE XXXII, NO_x Field Test Data Summary (ppm NO_x, $\bar{X} \pm s$)

	Hercules (1)	Hercules (2)	Moapa (Coal)	Diesel (Oil)	Boiler (Gas)	Std. (211 ppm)
Tube						
SIE	581±68	510±90	576±38	372±23	16±1.7	204±3
PDS	599±41	553±132	571±73	335±58	20±4	$221\pm^{13}_{23}$
Flask						
SIE	--	544±142	638±43	438±36	--	257±10
PDS	602±66	576±141	621±82	368±21	--	206±2

This data summary shows the mean and standard deviation of each sampling/analysis method combination for all of the field tests. Repeated also is the data from Table XXVII for comparison. At this point, it should be recognized that each field test represents a unique situation and only the data for a single field test can be compared with respect to analysis and sampling bias. The combustion sources showed the lowest NO_x level variability as evidenced by the lower standard deviations. The high standard deviations for the Hercules No. 2 Flask data clearly show the need for a continuous sampling method for highly variable sources. Use of the extended grab sampling technique (Hercules No. 1) greatly improved the agreement between the means of the sampling methods. The effect of condensable moisture on the analysis results is apparent with the Moapa Flask data. Moisture condensation in the flasks leads to gas samples which are larger than those which can be calculated from flask volumes. Apparently there was less moisture in the diesel exhaust because the Flask/PDS and Tube/SIE data agree quite well. The unburned diesel oil

condensed on the walls of the flasks but since it was likely an aerosol in the first place, it did not contribute to the sample size measurement error. The excellent agreement between this Flask/PDS and Tube/SIE data also indicates that unburned hydrocarbons do not seriously interfere with the PbO_2 tube sampling method. A series of "paired t" tests was performed using the hypothesis that the means of the various Sample Method/Analysis Method combinations for each field test were equal at the 95% confidence level. This data is shown in Table XXXIII.

TABLE XXXIII, "Paired t" Results at 95% Level

Sample/Analysis Methods	Hercules(No. 2)	Moapa	Diesel	Boiler
Flask/PDS vs Tube/SIE	-	-	+	
Tube/PDS vs Tube/SIE	-	+	-	-
Flask/PDS vs Tube/PDS	-	-	-	

- Significantly different at 95% level

+ Not significantly different at 95% level

The Flask/SIE data is not compared since an analysis bias is definitely shown to exist (Table XXVI). No explanation can be offered for the Hercules data except that the inequalities are due to the high standard deviations shown in Table XXXII. The Moapa data illustrates the significance of the sampling method when condensable moisture is present. The data from the Diesel engine shows that when condensable moisture is absent and the source is constant, the tube/SIE method is equivalent to the flask/PDS method. The inequality demonstrated with the boiler data can only be explained by the loss in analysis accuracy at extremely low NO_x levels.

In summary, the tube/SIE method is numerically equivalent to Method 7 (3) for the Diesel generator test. The lack of equivalency for the Hercules nitric acid plant and the Moapa power generator was shown to be due to uncorrected errors in the flask sample. If the errors were determined and the results corrected, the numerical equivalency would probably hold for those sources also. Thus it is obvious that the tube/SIE method can be recommended as a replacement for and an improvement over the current Method 7.

5.0 Theoretical Considerations

5.1 Discussion of reactions between proposed flue gas substances and crystalline lead dioxide.

In Table XXXIV are given proposed reactions between a number of probable flue gas substances with lead dioxide along with enthalpy and free energy values (20). Since the chemistry of most of the reactions have never been observed in detail, some of the proposed interactions may not occur in practice. However, the free energies and possibly the enthalpies of the reactions of Table XXXIV may be used as guides for predicting whether or not absorption of the probable flue gas materials will occur.

Data have been accumulated that show nitric oxide, nitrogen dioxide, carbon monoxide, and sulfur dioxide to be absorbed by electrolytic lead dioxide while carbon dioxide is unabsorbed. The free energies of reaction between lead dioxide and nitrogen dioxide, carbon monoxide, or sulfur dioxide all exceed minus forty-two kilocalories per mole. A most interesting anomaly occurs when the free energies of reaction of nitric oxide and carbon

dioxide with lead dioxide are compared. While both free energies are negative, the more negative value lies with absorption of carbon dioxide. Carbon dioxide absorption does not take place under the usual experimental conditions (temperatures ranging between room temperature and 185°C). In general chemical experience, reactions that have large free energies usually occur under relatively mild conditions, but reactions that have small free energies may be unlikely to occur under the same conditions. Thus, quantitative absorption of nitric oxide by lead dioxide would be predicted to be unlikely on the basis of the small free energy involved and the observation that carbon dioxide with a more negative free energy of reaction is unaffected under identical experimental conditions. From this and other data that have been obtained, Reaction 1 of Table XXXIV originally proposed by Mishmash and Meloan (4) may be an incorrect description of the interaction between nitric oxide and electrolytic PbO_2. This subject will be discussed in more detail later.

TABLE XXXIV, Thermochemical Data

Probable Reactions between Flue Gas Species and PbO_2	Absorption?	ΔH_{298} Kcal/mole PbO_2	ΔF_{298} Kcal/mole PbO_2
1. $NO + PbO_2 \rightarrow NO_2 + PbO$	yes	- 1.53	- 2.81
2. $2NO_2 + PbO_2 \rightarrow Pb(NO_3)_2$	yes	-58.16	-42.
3. $CO + PbO_2 \rightarrow PbCO_3$	yes	-76.3	-66.1
4. $CO_2 + PbO_2 \rightarrow PbCO_3 + \frac{1}{2} O_2$	no	-16.7	- 4.7
5. $SO_2 + PbO_2 \rightarrow PbSO_4$	yes	-84.0	-71.38
6. $SO_3 + PbO_2 \rightarrow PbSO_4 + \frac{1}{2} O_2$	unknown	-60.36	-54.43
7. $2HF + PbO_2 \rightarrow PbF_2 + H_2O(g) + \frac{1}{2} O_2$	unknown	-23.81	-16.17
8. $2HCl + PbO_2 \rightarrow PbCl_2 + H_2O(g) + \frac{1}{2} O_2$	yes	-35.33	-33.70
9. $2HCl(l) + PbO_2 \rightarrow PbCl_2 + H_2O + \frac{1}{2} O_2$	unknown	- 9.93	- 8.61
10. $Cl_2(g) + PbO_2 \rightarrow PbCl_2 + \frac{1}{2} O_2$	unknown	-21.65	-24.62
11. $2HBr + PbO_2 \rightarrow PbBr_2 + H_2O + \frac{1}{2} O_2$	unknown	-41.91	-40.42
12. $2HNO_3 + PbO_2 \rightarrow Pb(NO_3)_2 + H_2O(g) + \frac{1}{2} O_2$	unknown	-35.94	-36.4
13. $2HNO_3(l) + PbO_2 \rightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2} O_2$	no	- 9.01	---
14. $H_2SO_4 + PbO_2 \rightarrow PbSO_4 + H_2O + \frac{1}{2} O_2$	unknown	-18.20	-32.83
15. $H_2SO_4(l) + PbO_2 \rightarrow PbSO_4 + H_2O + \frac{1}{2} O_2$	no	+ 4.15	---
16. $\frac{1}{2}SiF_4 + PbO_2 \rightarrow PbF_2 + \frac{1}{2}SiO_2 + \frac{1}{2} O_2$	unknown	-12.05	- 7.15

Since hydrogen chloride is absorbed by electrolytic lead dioxide, nitric and sulfuric acid vapors should also be absorbed because of the similarity of the free energies of reaction. However, aqueous nitric and sulfuric acids do not react with lead dioxide at temperatures up to the boiling point of water, and the thermodynamic values of the enthalpy and free energy for these reactions are much lower than for the gaseous acid vapors. Lead dioxide should also be unaffected by aqueous hydrochloric acid since the enthalpy and free energy values for such an interaction is very similar to those with nitric acid.

From this brief inspection of the thermodynamic values it appears that those materials having free energies of reaction with lead dioxide greater than -30 kilocalories per mole are readily absorbed. Those materials whose free energies of reaction with lead dioxide are less than -10 kilocalories per mole do not appear to interact under normal experimental conditions.

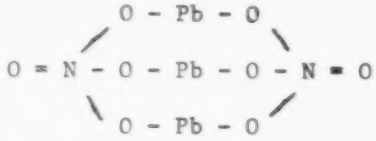
As yet, it is unknown whether or not materials with free energies of reaction with lead dioxide with intermediate values(hydrogen fluoride) will be absorbed or not. The glaring anomaly with this simple reasoning is the fact that nitric oxide is quantitively absorbed. However, it is interesting, where experimental data is available, that acid vapors will be absorbed while the aqueous solutions are inactive to lead dioxide.

The outstanding feature in the application of lead dioxide to flue gas analysis is its surprising ability to quantitatively absorb nitric oxide at low concentrations. However, amorphous lead dioxide and other commercial forms of lead dioxide will not quantitatively absorb nitric oxide.

Inertness of lead dioxide to nitric oxide is indicated by the free energy of reaction as was discussed above. The night-and-day aspect of the reactivity of amorphous lead dioxide and electrolytic α and/or β lead dioxide with nitric oxide demonstrates that an unusual chemical reaction is obtained with the electrolytic materials. X-ray diffraction scans of the powder obtained before and after saturation of the "reactive" lead dioxide with nitric oxide indicates that no new crystalline material is formed. That is, the product formed by reaction between nitric oxide and "reactive" lead dioxide is amorphous. X-ray scans after saturation of the lead dioxide with nitrogen dioxide definitely show the presence of crystalline lead nitrate. Infrared spectra (5000 cm^{-1} to 625 cm^{-1}) before and after saturation of the "reactive" lead dioxide with nitric oxide exhibits the appearance of a very broad band at 1340 cm^{-1} which is not the same shape as the principal nitrate absorptions in lead nitrate near the same wavelength, and other small bands are missing. Nitrogen dioxide saturated electrolytic lead dioxide, however, does give an infrared spectrum identical with lead nitrate. Treatment of the nitric oxide saturated lead dioxide with water yields nitrate ion. Additionally, the capacity of the "reactive" lead dioxide is surprisingly high, up to 75% or more of that predicted by equations 1 and 2 of Table XXXIV. Thus, no coating or passivation of the lead dioxide surface occurs to an appreciable degree.

The extraordinary reactivity of carefully prepared electrolytic lead dioxide with nitric oxide must arise from a chemical reaction different from that proposed by Mishmash and Meloan (4). The data reported above shows that lead nitrate is not a primary product of reaction between nitric oxide and lead dioxide although nitrate is formed through later hydrolysis.

The nitric oxide reaction is with α or β-crystalline lead dioxide and not amorphous lead dioxide. One possible explanation of the nitric oxide reaction would be that nitric oxide inserts between two or, preferably, three oxygen atoms of the crystalline lead dioxide forming two or three oxygen nitrogen bonds simultaneously in a bridged structure. An intermediate material with a structure such as,



could explain the observations that were made. This model compound fits the data for the following reasons: (a) such an insertion mechanism as described above readily explains why amorphous lead dioxide, lacking the necessary geometric array of oxygen atoms, will not interact with nitric oxide, while the proper crystalline forms of lead dioxide are highly reactive; (b) if three nitrogen to oxygen bonds are formed simultaneously by an insertion, the energetics are roughly similar to direct conversion of nitric oxide to nitrate; (c) the unusual infrared spectrum could be explained by such an intermediate; (d) an intermediate such as shown above could be expected to form nitrate ion during hydrolysis; (e) such an intermediate could be expected to separate out from the lead dioxide crystal leaving a fresh active surface which explains the high capacity; (f) such an intermediate results in the same overall stoichiometry as indicated by the combination of equations 1 and 2 of Table XXXIV; e.g., $3PbO_2 + 2NO \rightarrow Pb(NO_3)_2 + 2PbO$. Postulation of a rather unusual bridged structure explains the data obtained, but final verification awaits the isolation and identification of the crystalline lead dioxide-nitric oxide intermediate.

III - SUMMARY AND CONCLUSIONS

The grab sampling technique/PDS analysis method for NO_x described in the Federal Register has been evaluated and several critical deficiencies were discovered: (a) use of the grab sampling technique requires that many samples must be taken from a stationary source to accurately define the 24 hour emission level; (b) the acidic H_2O_2 absorbing reagent in the sample flask necessitates the use of NaOH for neutralization and introduces sufficient CO_3^{2-} during the analysis to give erratic and erroneously low results; (c) during the evaporation step, silica from the glassware is dissolved and later produces particulate matter which, upon filtration, gives low results; (d) no provision for removal of interfering substances such as Cl^- is mentioned.

A modified PDS analysis scheme is presented in Appendix I which minimizes some of the foregoing deficiencies through the use of a neutral H_2O_2 absorbing reagent and platinum crucibles for sample evaporation. Remaining, however, are the sampling and interference problems.

In order to overcome the problems that are inherent with grab sampling techniques, a search was conducted for a means of sampling NO_x on a relatively continuous basis. The principal oxide of nitrogen emitted from stationary sources is NO which unfortunately is a relatively stable and insoluble species. A number of liquid absorbing solutions and systems were evaluated, but all proved to be ineffective as continuous sampling devices for NO. The solid sorbent, PbO_2, was found to quantitatively absorb NO and NO_2 (by converting both to $Pb(NO_3)_2$). During the initial studies of this solid sorbent it was determined that the crystal form of the PbO_2 was critical to its reactivity toward NO. The results of x-ray

crystallographic analyses identified the electrolytically derived PbO_2 (α and β crystal forms) as the only NO reactive source of this solid sorbent. A time-integrated sampling scheme for NO_x was successfully developed and evaluated which uses PbO_2 as the solid sorbent. In addition, the Orion NO_3^- Selective Ion Electrode (SIE) was used successfully as the analytical device for measurement of NO_3^- in the aqueous PbO_2 extract. A complete sampling and analysis scheme for NO_x which describes a PbO_2 time-integrated sampler and a SIE analysis method is detailed in Appendix II.

Although PbO_2 absorbs other combustion products such as SO_2, CO, and HCl which can interfere with the SIE, the analysis scheme presented describes a simple selective precipitation technique which virtually eliminates the possibility of other anion interferences.

Similar techniques for elimination of anion interferences were developed for the grab sample/PDS method (Appendix III) and field tests were conducted to evaluate the performance of the two sampling and analysis schemes. The field tests consisted of NO_x emission measurements of a nitric acid plant, a coal fired power plant, a gas fired boiler, and a diesel engine exhaust. During the field tests, grab samples and PbO_2 time-integrated samples were collected simultaneously and both SIE and PDS analyses were performed on the collected samples. In all cases the precision of the results reflected the advantages of the time-integrated PbO_2 sample/SIE combination. An additional feature of this sample technique was demonstrated by the gas fired boiler tests where the NO_x emission level was insufficient for the collection of an adequate flask sample whereas by simply lengthening the sampling time, adequate NO_x was collected in the PbO_2 sampler for analysis by both the SIE and PDS methods.

While all objectives of the program were met there are some important additional benefits and features which cannot be overlooked: (a) the overall cost of an NO_x analysis in time and manhours has been appreciably reduced by the PbO_2 tube/SIE sampling/analysis system. For example, five tube samples of a stationary source effluent can be obtained in about three hours. The analysis of the samples requires another hour of laboratory time so that final calculations could be finished within a half an hour more. The 16 (or more) hour waiting period requirement of the flask sample is eliminated as is the more lengthy and tedious PDS analysis; (b) the PbO_2 tube sampling device lends itself to interlaboratory comparisons because an issuing laboratory can expose a number of tubes to a standard NO source, mail them to recipients, and have μg NO_3^- results for calculations within a very short time; (c) the accuracy, precision, and sensitivity of the PbO_2 tube sampling device have been reported in Section 3.0 of the Technical Discussion. The unique character and specificity of α and β PbO_2 for the quantitative reaction with NO from 25°C to 190°C is of significance. An added feature is the relatively large capacity of this material for NO and NO_2 absorption. These factors in addition to insensitivity to unburned hydrocarbons argue strongly for its consideration also as an NO_x sampling device for mobile and ambient air sources (see Appendix IV); (d) while HCl, HF, SO_2, and CO are apparently absorbed and initially caused some analysis problems during the program, the "reactivity" of α and/or β PbO_2 can possibly be utilized for their analysis in combustion stack gases. This could perhaps be accomplished by using a strong PO_4^{3-} solution in order to release the various anions from Pb^{2+} for subsequent separation and quantitative determination. Development of this possibility into an acceptable analysis scheme needs further effort.

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Appendix I

Recommended Changes to Method 7

(Fed. Register, Vol. 36, No 247, Part II, dated 23 Dec 71)

1. Principle and Applicability

1.1 Principle. A grab sample is collected in an evacuated flask containing a neutral 3% hydrogen peroxide absorbing solution and the nitrogen oxides, except for nitrous oxide, are measured colorimetrically using the phenol-disulfonic acid (PDS) procedure.

1.2 to 2.2.3 inclusive: no changes

2.3 Analysis

2.3.1 Steam bath or resistance heated hot plate.

2.3.2 Platinum or gold-plated nickel crucibles (15-25 ml size), one for each sample, standard and reagent blank.

2.3.3 Volumetric pipettes, 1 ml, 2 ml, 5 ml, 10 ml.

2.3.4 Transfer pipette, 10 ml with 0.1 ml graduations.

2.3.5 Volumetric flasks, 100 ml, one for each sample, standard and reagent blank, 1000 ml for std. solution.

2.3.6 Spectrophotometer, narrow band, to measure absorbance at 410-420 nm.

2.3.7 Graduated cylinder, 100 ml, 1 ml graduations.

2.3.8 Analytical balance, 100g capacity, 0.1 mg sensitivity.

2.3.9 Ice bath - 1 liter plastic beaker and chipped ice + H_2O.

3. Reagents

3.1 Sampling

3.1.1 Absorbing solution - Dilute 100 ml of 30% hydrogen peroxide to 1 liter with distilled water. Mix well and store in a clean bottle away

from heat and light. Prepare a fresh solution weekly.

3.2 to 3.3.3 inclusive: no change

3.3.4 Standard solution - Dissolve exactly 2.1980g of dried potassium nitrate (KNO_3) in distilled water and dilute to 1 liter in a 1000 ml volumetric flask (1 ml = 1000 μg NO_2). For the working standard, dilute 10 ml to 100 ml with distilled water in a 100 ml volumecric flask (1 ml = 100 μg NO_2). Store both solutions in screw-capped plastic containers.

3.3.5 to 4.1.1 inclusive: no changes

4.2 Sample Recovery

4.2.1 Connect the flask to a mercury-filled U-tube manometer, open the valve from the flask to the monometer and record the flask pressure, temperature and barometric pressure. Allow the flask to stand for a minimum of 16 hours and shake the contents for 2 minutes. If the contents of the flask are to be shipped, transfer the 25 ml to a dry plastic container (bottle). Add 5 drops 1N NaOH prior to shipping.

4.3 Analysis

4.3.1 Place 1 drop of 1N NaOH into each of the platinum or gold-plated nickel crucibles. Pipet 5 ml of the peroxide absorbing solution into one crucible for a reagent blank. Pipet a 1/5 (one fifth) aliquot of the sample solution into another crucible (5 ml for a non-shipped sample and 10 ml from a shipped sample after adjusting its volume to 50 ml). Allow the peroxide decomposition to proceed at room temperature for 5-10 minutes. Place the crucibles on a 100°C hot plate or steam bath and evaporate solutions to dryness. Remove the crucibles and allow to cool, and add 2 ml of the PDS reagent. Allow 5 minutes for dissolution of solids

(tilt and rotate the crucible to wet the walls with PDS). Transfer the PDS solution from the crucible to a 100 ml volumetric flask, rinsing 3 or 4 times with ~ 10 ml portions of distilled water. Use a plastic funnel. Place the 100 ml volumetric flask into an ice bath and slowly add 8 ml concentrated NH_4OH(28% NH_3) with swirling. Make up to the mark with distilled water and mix thoroughly. Set the spectrophotometer to "0" absorbance (100%T) at 410-420 nm with a 1 cm cell containing the blank which was treated the same as the sample. Record the absorbances of the yellow sample solutions in a 1 cm cell. Determine the μg NO_2/100 ml for the aliquot from a previously or concurrently prepared calibration curve.

5. to 5.1 inclusive: no changes

5.2 Spectrophotometer Calibration - Add 0.0 ml, 1.0 ml, 2.0 ml, 3.0 ml and 4.0 ml of the nitrate (100 μg NO_2 = 1 ml) working standard solution to each of five (5) crucibles. Add 1 drop of 1 N NaOH plus 5 ml of the peroxide absorbing solution. Evaporate the solutions on a hot plate or a steam bath and continue the procedure of section 4.3. Plot the absorbances of the standards on linear graph paper and draw a smooth line through the origin. The slope should be 0.15 ± 0.007 absorbance per 100 μg NO_2/100 ml. Calculate the total μg NO_2 per sample as follows:

$$M = a \times F$$

where M = Total μg NO_2 (sec 6.2)

a = μg NO_2/100 ml from calibration curve

F = aliquot factor (i.e., 25/5, 25/10, etc.)

Appendix II

Determination of Nitrogen Oxide Emissions from Stationary Sources

1. Principle and Applicability

1.1 Principle. A gas sample is slowly drawn through a heated glass tube containing an active form of lead dioxide thereby converting the nitrogen oxides, except nitrous oxide to lead nitrate. The lead nitrate is extracted with water and the nitrate ion concentration is measured with the Nitrate Selective Ion Electrode.

1.2 Applicability . . . . . .

2. Apparatus

2.1 Sampling. See Figure 1.

2.1.1 Probe - Borosilicate glass, heated. Heating is unnecessary if the dewpoint of the sample gas is equal to or below ambient temperature.

2.1.2 Air Pump - Equipped with inlet filter and water separator. Capable of pumping 20-50 standard liters/min.

2.1.3 NOx absorption tube - Borosilicate glass, ¼ in. O.D. (6 mm) and packed with 2-4g of 30/50 mesh PbO_2. The granular PbO_2 is held in place with borosilicate glass wool plugs.

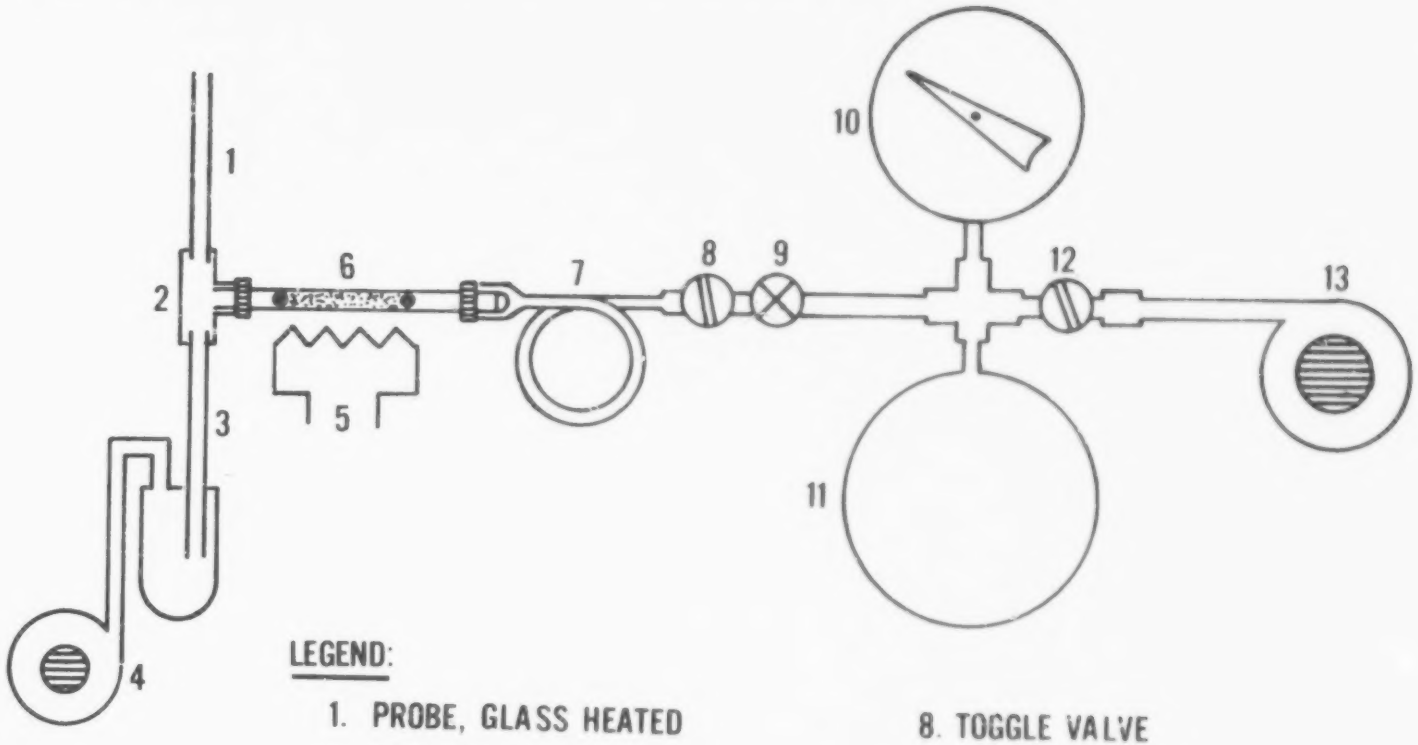
2.1.4 Compression Fitting - For ¼ in. O.D. (6 mm) tubing, either "O"-ring or polytetrafluoroethylene ferrule type, vacuum tight, 2 required for glass to metal seals.

2.1.5 Tube furnace or heater - capable of maintaining 100-180 ± 10°C.

2.1.6 Flow Control Valves - Vacuum tight - A shut off valve followed by a fine metering valve. System should be capable of flow control from 10-200 cc/min at one atmosphere pressure differential.

Figure 1

SAMPLING APPARATUS



LEGEND:

1. PROBE, GLASS HEATED
2. SAMPLING TEE, S/S
3. WATER/PARTICULATE TRAP, GLASS
4. AIR PUMP
5. TUBE FURNACE OR HEATER
6. PbO_2 SAMPLING TUBE, WITH COMPRESSION FITTINGS
7. 1/16 IN. O.D. TUBING, S/S
8. TOGGLE VALVE
9. METERING VALVE
10. ABS. PRESS. GAUGE OR Hg MANOMETER
11. BALLAST, METAL, 5 LITER CAPACITY
12. VACUUM VALVE
13. VACUUM PUMP

2.1.7 Pressure Gauge - Absolute pressure gauge calibrated in 1 mm increments from 0-760 mm or a similarly equipped mercury "U-tube" manometer.

2.1.8 Ballast Volume - Metal, thin wall, approximately 5 liter volume for NOx sources of 50-1000 ppm. A larger volume should be substituted if the source contains $<$50 ppm NOx.

2.1.9 Vacuum Valve - Vacuum tight, bellows seal.

2.1.10 Vacuum Pump - Two stage, 50 liter/minute capacity, ultimate vacuum capability of 0.1 mm Hg or better.

2.1.11 Thermometer - 0-100°C range, 1°C graduations.

2.2 Sample Recovery

2.2.1 Centrifuge Tube - Borosilicate glass, 12 ml capacity and equipped with a screw cap, one for each absorption tube.

2.2.2 Microspatula - sized to fit inside the absorption tube.

2.2.3 Stirring rod - sized to fit inside the absorption tube but somewhat longer.

2.2.4 Syringe - 10 ml capacity, 0.2 ml graduations.

2.2.5 Hot Plate - 36 sq in. heating surface, capable of boiling water.

2.2.6 Beaker - Borosilicate glass, 2 required, for boiling water and for ice bath, 600 ml capacities.

2.2.7 Clinical Centrifuge - Head cavities sized to fit 12 ml centrifuge tubes, 2500 rpm capability.

2.2.8 Test tube rack - to fit 12 ml centrifuge tubes.

2.2.9 Plastic Bottle - Polyethylene, narrow mouth, screw capped, 100 ml.

2.3 Analysis

2.3.1 Syringe - 250 µl (0.250 ml) capacity, 10 µl (0.01 ml) graduations.

2.3.2 Beaker - Plastic, disposable, 25 ml capacity, one for each sample and calibration standard.

2.3.3 Volumetric pipettes - 2, 3, 5, 10, 50 and 100 ml capacities.

2.3.4 Volumetric flasks - 2-100 ml, 6-1000 ml.

2.3.5 Plastic Bottles - Polyethylene, narrow mouth, screw-capped, 2-100 ml, 6-1000 ml.

2.3.6 Nitrate Selective Ion Electrode, and kit for regeneration of electrode.

2.3.7 Ag/AgCl - Reference electrode, and AgCl/KCl filling solution.

2.3.8 Analytical balance - To measure to 0.1 mg.

2.3.9 Electrometer Amplifier - With millivolt readout, readable to 1 mv.

3. Reagents

3.1 Sampling

3.1.1 Lead Dioxide - 30/50 mesh, electrolytically derived [1] and purified according to Pregl [2].

3.2 Sample Recovery

3.2.1 Lead Fluoride - Anhydrous, purified, nitrate free.

3.2.2 Phosphate Buffer - Dissolve 20g of ACS reagent grade $Na_3PO_4 \cdot 12H_2O$ in 80g (ml) of distilled water. This is nearly a saturated solution therefore gentle heating of the mixture may be necessary. When dissolved, transfer the solution to a 100 ml plastic bottle. Minimize exposure of this solution to the atmosphere to prevent CO_2 absorption.

3.3 Analysis

3.3.1 2000 ppm PO_4^{3-} solution - Dissolve 0.800 g of ACS reagent grade $Na_3PO_4 .12H_2O$ in distilled water contained in a 100 ml volumetric flask, and dilute to the mark. Mix and transfer the contents of the flask to a 100 ml plastic bottle.

3.3.2 1000 ppm PO_4^{3-} solution - Dissolve 4.002 g of ACS reagent grade $Na_3PO_4 .12H_2O$ in distilled water contained in a 1000 ml volumetric flask and dilute to the mark. Mix and transfer the contents of the flask to a 1000 ml plastic bottle. At least 6000 ml will be required.

3.3.3 10,000 ppm NO_3^- Standard - Dissolve 2.6708g of dried ACS reagent grade $Pb(NO_3)_2$ in distilled water contained in a 100 ml volumetric flask and dilute to the mark. Mix and transfer the contents of the flask to a 100 ml plastic bottle.

3.3.4 NO_3^- Selective Ion Electrode calibration solutions.

3.3.4.1 1000 ppm NO_3^- Standard - Pipette 10.0 ml each of the 10,000 ppm NO_3^- standard and the 2000 ppm PO_4^{3-} buffer solution into a 1000 ml flask and dilute to the mark with 1000 ppm PO_4^{3-} buffer solution. Mix and transfer the contents of the flask to a 1000 ml plastic bottle.

3.3.4.2 500 ppm NO_3^- Standard - Pipette 5.00 ml each of the 10,000 ppm NO_3^- standard and the 2000 ppm PO_4^{3-} buffer solution into a 1000 ml volumetric flask and dilute to the mark with 1000 ppm PO_4^{3-} buffer solution. Mix and transfer the contents of the flask to a 1000 ml plastic bottle.

3.3.4.3 300 ppm NO_3^- Standard - Pipette 3.00 ml each of the 10,000 ppm NO_3^- standard and the 2000 ppm PO_4^{3-} buffer solution into a 1000 ml volumetric flask and dilute to the mark with the 1000 ppm PO_4^{3-} buffer solution. Mix and transfer the contents of the flask to a plastic bottle.

3.3.4.4 200 ppm NO_3^- Standard - Pipette 2.00 ml each of the 10,000 ppm NO_3^- standard and the 2000 ppm PO_4^{3-} buffer solution into a 1000 ml volumetric flask and dilute to the mark with the 1000 ppm PO_4^{3-} buffer solution. Mix and transfer the contents of the flask to a 1000 ml plastic bottle.

3.3.4.5 100 ppm NO_3^- Standard - Pipette 100.0 ml of the 1000 ppm NO_3^- standard into a 1000 ml volumetric flask and dilute to the mark with the 1000 ppm PO_4^{3-} buffer solution. Mix and transfer the contents of the flask to a 1000 ml plastic bottle.

3.3.4.6 50 ppm NO_3^- Standard - Pipette 50.0 ml of the 1000 ppm NO_3^- standard into a 1000 ml volumetric flask and dilute to the mark with the 1000 ppm PO_4^{3-} buffer solution. Mix and transfer the contents of the flask to a 1000 ml plastic bottle.

4. Procedure

4.1 Sampling

4.1.1 Assemble the probe and air pump as shown in Figure 1 but with the sample inlet side arm capped. Insert the probe into the sample port and turn on the air pump so that sample gas is drawn through the system at 20-50 liters/min. Heat the probe to approximately the sample gas temperature if the dewpoint of the gas is above ambient temperature. Allow the system to purge for several minutes before continuing. Insert a sample absorption tube into the heater (adjusted to 100 - 180 ± 10°C) and connect the tube to the flow control valves as shown. With the toggle valve closed, open the vacuum valve and evacuate the ballast volume and pressure gauge (or manometer). Close the vacuum valve and record the initial pressure (Po).

Po should be constant for at least 20 min. to insure that the system is free from leaks. If no leak is detected connect the sample absorption tube to the sample probe side arm. Open the toggle valve and adjust the metering valve to the desired sampling rate (determined by the rate of pressure increase in the ballast volume). After the desired sample size has been accumulated, close the toggle valve and remove the sample absorption tube. Record the final pressures (P_f) in the ballast volume and ambient temperature. In addition, use the gauge (or manometer) to determine the barometric pressure. The volume of the ballast vessel and the sample volume should be correlated with the moisture and NOx content of the sample gas such that adequate NOx for analysis can be collected without exceeding a partial pressure of water vapor in the ballast volume whereby condensation will occur. Evacuate the ballast volume and repeat the sequence for subsequent samples. The sample absorption tubes should always be protected from atmospheric contamination because the PbO_2 will absorb NOx even at ambient temperature.

4.2 Sample Recovery

4.2.1 Remove one glass wool plug with a microspatula from the sample absorption tube and transfer it and the PbO_2 to a centrifuge tube. Remove the remaining plug by pushing it through with a stirring rod in the same direction so that the PbO_2 adhering to the inside wall of the tube is also transferred to the centrifuge tube. With a microspatula add approximately 0.1 g of PbF_2 to the contents of the centrifuge tube. Use a 10 ml syringe to transfer 8.0 ml of distilled water to the mixture and cap the centrifuge tube securely. Thoroughly mix the contents of the centrifuge

tube and place it in boiling water. Allow the slurry to remain at $\sim 100^{o}C$ for 15-30 minutes with occasional mixing. After the heating period, cool the slurry to $0^{o}C$ in an ice bath. Allow the tube to cool for 15-30 minutes and then centrifuge the mixture at ~2500 rpm for 5-10 minutes. Remove the tube from the centrifuge and place it in a test tube rack. Allow the contents of the centrifuge tube to return to ambient temperature and decant the supernatant liquid into a disposable beaker. Add 150 µl (0.15 ml) of 5% PO_4^{3-} buffer to the contents of the beaker and swirl the mixture.

4.3 Analysis

4.3.1 Immerse the Nitrate Selective Ion Electrode and the Ag/AgCl reference electrode in the buffered solution and rotate the beaker several times to remove any gas bubbles which may be adhering to the electrodes. Allow the millivolt meter to stabilize (~30 sec.) and record the millivolt reading. Compare the reading with the calibration curve prepared in Section 5.2 to determine the nitrate ion concentration of the sample solution and use the formulas in Sections 6.2 and 6.3 to calculate the NOx concentration of the gas sample.

5. Calibration

5.1 Sampling Apparatus (Figure 1)

5.1.1 With the toggle valve closed open the vacuum valve and evacuate the apparatus. Following evacuation, close the vacuum valve and disconnect the vacuum line from the vacuum valve. Record the system Pressure (Po) and connect a 1 to 10 liter vessel containing dry air at one atmosphere pressure to the vacuum valve. The water volume of the vessel should be previously determined. Open the vacuum valve and record the equilibrium pressure (P_f). Also record the barometric pressure. Use the formula in Section 6.1 to determine the system volume.

5.2 Nitrate Selective Ion Electrode (SIE)

5.2.1 Rinse the SIE and reference electrode with distilled water and dry with a clean tissue. In turn, starting with the most dilute NO_3^- standard, transfer approximately 10 ml to a clean plastic disposable beaker and immerse the electrodes in the liquid. Rotate the beaker several times to remove any gas bubbles which may adhere to the electrodes and allow approximately 30 seconds for the millivolt meter to stabilize. Record the millivolt reading and the corresponding NO_3^- concentration. Remove the beaker, wipe the electrodes with a clean tissue, and proceed to the next most concentrated standard without rinsing the electrodes. Plot log NO_3^- concentration vs millivolt reading (use of semilog graph paper is most convenient). After the millivolt reading for the most concentrated NO_3^- standard is recorded, place the dried electrodes in one of the NO_3^- standards which approximates the NO_3^- concentration of the sample. This serves both to check the stability of the electrode and also decrease the equilibration time of the electrode with the sample solution. Do not readjust the calibration of the meter until the reading has been checked several times with fresh solutions of the more dilute NO_3^- standard. Once calibrated, the electrodes should only be carefully wiped with a clean tissue between each standard and each sample. In the event that the millivolt reading cannot be adjusted to the normal value for a given standard or that the reading drifts continuously, the electrode should be reconditioned in accordance with the manufacturer's instructions.

6. Calculations

6.1 Sampling apparatus volume.

$$V_a = \left(\frac{Pbp\ Vs}{P_f - P_o}\right) - V_s$$

equation 1

where:

Va = sampling app. vol (liters)
Vs = water vol. of std. (liters)
Pbp = barometric pressure (mmHg)
P_o = initial pressure (mmHg)
P_f = final pressure (mmHg)

6.2 Gas Sample Volume.

$$Vg = \left(\frac{P_f - P_o}{Pbp}\right) Va$$

equation 2

where:

Vg = gas sample volume (liters)
Va = sampling app. vol (liters)
Pbp = barometric pressute at sample site (mmHg)
P_f = final apparatus pressure (mmHg)
P_o = initial apparatus pressure (mmHg)

6.3 NOx concentration.

$$C = \frac{AFR}{VgM}$$

equation 3

where:

A = ppm NO_3^- in sample solution
$F = 8.0\ ml \times \frac{7.0 + 0.15}{7.0} = 8.17\ ml$
$R = 22.4 \times \frac{760}{Pbp} \times \frac{T}{273}$, T = ($^oK$) at sample site, PbP = (mmHg) barometric pressure at sample site
Vg = sample volume (liters)
M = formula wt. NO_3^- (62.01)

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Appendix III

The following procedure is designed to determine µg nitrate ion in the presence of chloride ion when Method 7 flask samples have been obtained. It is important that the final sample pressure measurement be made at the end of paragraph 4.1.1., and prior to allowing the sample to stand for a minimum of 16 hrs. Assuming that HCl was a stack gas constituent and the 25 ml absorbing solution is neutral 3% H_2O_2, the modified analysis begins with paragraph 4.3, while apparatus and reagent additions are listed in paragraphs 2.3 and 3.3. The reaction with phenoldisulfonic acid takes place in an aqueous medium which helps prevent loss of NO_x by volatilization as NOCl.

2.3 Analysis

2.3.1 Steam bath or resistance heated hot plate.

2.3.2 Beakers, 50 ml size, one for each sample, standard and reagent blank.

2.3.3 Volumetric pipettes, 1, 2, 5, 10, 20 ml.

2.3.4 Transfer pipette, 10 ml with 0.1 ml graduations.

2.3.5 Plastic bottles, about 75 ml size, one for each sample, std., and reagent blank, with screw cap.

2.3.6 Volumetric flasks, 1000 ml for Std. solutions, 25 ml and 100 ml one for each sample, std., and reagent blank.

2.3.7 Spectrophotometer, narrow band, to measure absorbance at 405-410 nm.

2.3.8 Graduated cylinder, 100 ml with 1 ml graduations.

2.3.9 Analytical balance, 100g cap., 0.1 mg sensitivity.

2.3.10 Ice bath, 1 liter, plastic or metal container.

2.3.11 Centrifuge, clinical, capable of accepting 12-15 ml conical tubes.

2.3.12 Centrifuge tubes, glass, 12-15 ml, one for each sample, Std., and reagent blank, with teflon seals in the screw cap.

3.3 Analysis

3.3.1 to 3.3.3 inclusive - no changes.

3.3.4 Standard Solution - Dissolve exactly 2.1980g of dried ACS Reagent grade potassium nitrate (KNO_3) in distilled water and dilute to the mark in a 1000 ml vol flask (1 ml = 1000 µg NO_2). The working standard is prepared by diluting 10 ml to 100 ml with distilled water in a 100 ml volumetric flask (1 ml = 100 µg NO_2).

3.3.5 to 3.3.6 inclusive - no changes.

3.3.7 Lead Dioxide, PbO_2, nitrate-free, electrolytically derived and prepared according to Pregl.

3.3.8 Lead Fluoride, PbF_2, nitrate-free, purified grade.

4. to 4.1 inclusive - no change, except to measure flask pressure at end of paragraph 4.1.1.

4.2 Sample recovery.

4.2.1 Let the flask stand for a minimum of 16 hours and then shake contents for 2 minutes. Remove flask valve stopper and carefully transfer contents to a 75 ml plastic bottle into which 5 drops of IN NaOH have been added. Use a plastic funnel. For a blank add 25 ml neutral H_2O_2 to another bottle with 5 drops of IN NaOH. Cap the bottle. The sample is now ready for shipment or analysis.

4.3 Analysis

4.3.1 Shake the plast bottle to remove condensed moisture from the sides. Carefully loosen the screw cap to allow gas pressure to escape,

and remove screw cap. Add approximately 0.1g PbO_2 powder to the solution and replace cap loosely and allow the H_2O_2 decomposition to proceed to completion. Transfer 20 ml to a 25 ml volumetric flask with a 20 ml volumetric pipette, dilute to the mark with distilled water and mix. Transfer a 10 ml aliquot with a 10 ml volumetric pipette to a 12-15 ml glass centrifuge tube to which has been added approximately 0.1g PbF_2, cap and shake. Cool the centrifuge tube to 0°C in an ice bath (∿ 10 mins.), remove and place into centrifuge. Centrifuge at 2000-3000 rpm for 10 minutes. Return the tube to the ice bath and remove a 5 ml aliquot into a 50 ml beaker. Add 1 drop IN NaOH, mix and place the beaker on a steam bath or hot plate (∿ 100°C) and evaporate to 1 or 2 ml. Remove the beaker and allow to cool. Add 2 ml of the phenoldisulfonic acid reagent. Mix gently and place on the steam bath or hot plate for a least 10 minutes. Remove and allow to cool. Transfer the solution to a 100 ml volumetric flask, rinsing 3-4 times with ∿ 10 ml portions of distilled water. Use a plastic funnel. Place the 100 ml volumetric flask into an ice bath, swirl, and slowly add 8 ml concentrated NH_4OH (28% NH_3) using a transfer pipet. Dilute the solution to the mark with distilled water and mix thoroughly. Set the spectrophotometer to "0" absorbance (100% T) at 405 to 415 nm with a 1 cm cell containing a reagent blank which was prepared in the same manner as the sample. Record the absorbance of the sample solution (yellow) using the same 1 cm cell. Determine the µg NO_2/100 ml for the aliquot from a previously or concurrently prepared calibration curve.

5. to 5.1 inclusive - no change.

5.2 Spectrophotometer. Add 0.0 ml, 1.0 ml, 2.0 ml, 3.0 ml and 4.0 ml of the nitrate working standard solution (100 µg NO_2 = 1 ml) to each of five plastic bottles containing 25 ml, 24 ml, 23 ml, 22 ml and 21 ml of neutral

3% H_2O_2. Add 5 drops of IN NaOH to each and mix. Continue the procedure as outlined in paragraph 4.3 by adding approximately 0.1g PbO_2 to each. Plot the absorbances of the standards on linear graph paper and draw a smooth curve through the origin. The slope should be 0.14 to 0.145 absorbance per 100 µg NO_2/100 ml. Calculate the total µg NO_2 per sample as follows:

$$m = 4a$$

where: m = total µg NO_2 (see para 6.2)

a = µg NO_2/100 ml from calibration curve

4 = aliquot factor (i.e., 20/5).

Appendix IV

Application of PbO_2 to Mobile Source and Ambient Air Sampling

I. Mobile Sources

1. NO_x concentration range. The stationary diesel engine which was tested (see Sec. 4.4) produced approximately 370 ppm NO_x. In addition, a 392 cu. in. 1970 automobile engine which used premium grade gasoline was tested (not reported in the text) at fast idle and no load. The average emission level for this source was 50 ppm. In view of the above, it seems reasonable to assume that mobile source NO_x emission levels should range between 10-1000 ppm.

2. Required Sampling Parameters. The greatest difficulty in sampling for NO_x will occur at the lowest emission levels (i.e., 10 ppm). At low emission levels large gas samples are required to collect sufficient NO_x for analysis with the S.I.E. By rearrangement of equation 6.3 (Appendix II), the necessary gas sample volume for an adequate NO_3^- concentration in the final solution can be determined. If 25 ppm NO_3^- is the lowest acceptable level for accurate analysis with the SIE, then using equation 6.3 the sample volume necessary for a 10 ppm NO_x source is:

$$Vg = \frac{AFR}{CM} = \frac{25x8x22.4}{10x62}$$

$$Vg = 7.2 \text{ liters}$$

If it is assumed that CO is the major competitor with NO_x for active sites on the PbO_2 and that only 75% of the theoretical PbO_2 capacity is available (see Sec. 5.1), then by using the CO/PbO_2 equation from Sec. 5.1 and the required sample volume (Vg) for 10 ppm NO_x it is possible to calculate

the highest CO level that can be tolerated when sampling a mobile source as follows:

$$\text{CO ppm} = \frac{WR}{M\ Vg}\ 0.75 \times 10^6$$

$$\text{CO ppm} = 39{,}000$$

where: W = 4g PbO_2/tube

M = 239g PbO_2/mole

R = 22.4 l/mole @ STP

Vg = 7.2 liters

Therefore, the PbO_2 tube (4g PbO_2) capacity will be exceeded if the source containing 10 ppm NO_x also contains 39,000 ppm CO (3.9%) when 7.2 liters of gas are sampled. A recent National Air Pollution Control Administration (NAPCA) publication (1) reports that the average CO emission level of an internal combustion engine is between 10,000 and 20,000 ppm (1-2%). In view of this data, the PbO_2 sampling tube can be used for mobile sources with at least a 100% safety factor even under the worst possible conditions.

II. Ambient Air

1. Mean NO_x Concentration. A much larger gas sample will be required for measurement of NO_x levels in ambient air since the mean level is much lower than the normal emission levels of both stationary and mobile sources. However, if a nominal NO_x level in ambient air is chosen, then the minimum sample size for SIE measurement can be calculated as before. At this point it must be recalled that PbO_2 reacts with both NO and NO_2 to form $Pb(NO_3)_2$. If 25 ppm NO_3^- is again chosen as the minimum acceptable level in the final

solution for SIE measurement, then the only remaining information necessary is a nominal ambient air NO_x level. Data summarized in a recent NAPCA report (2) shows that 0.05 ppm is a reasonable low nominal NO_x level for ambient air in U.S. cities. Use of the above and equation 6.3 defines the minimum gas sample size for accurate NO_x measurement.

$$Vg = \frac{AFR}{CM} = \frac{25x8x22.4}{0.05x62}$$

$$Vg = 1445 \text{ liters}$$

2. Sampler Configuration. The sample volume is not as unwieldy as it may seem if the collection time is expanded to a 24 hour period (i.e., $\frac{1445}{24x60}$ = 1 liter/min). With a modification in the sampler configuration, such as that depicted in Figure 1, sample collection should be relatively simple. On the basis of other NAPCA data (3) the major competitor with NO_x for active sites on the PbO_2 is again CO. A calculation for the maximum CO level which can be tolerated in a gas sample of 1445 liters is shown below:

$$CO\ ppm = \frac{WR}{MVg}\ 0.75 \times 10^6$$

where: W = 4g PbO_2

M = 239g PbO_2/mole

R = 22.4 l/mole @ STP

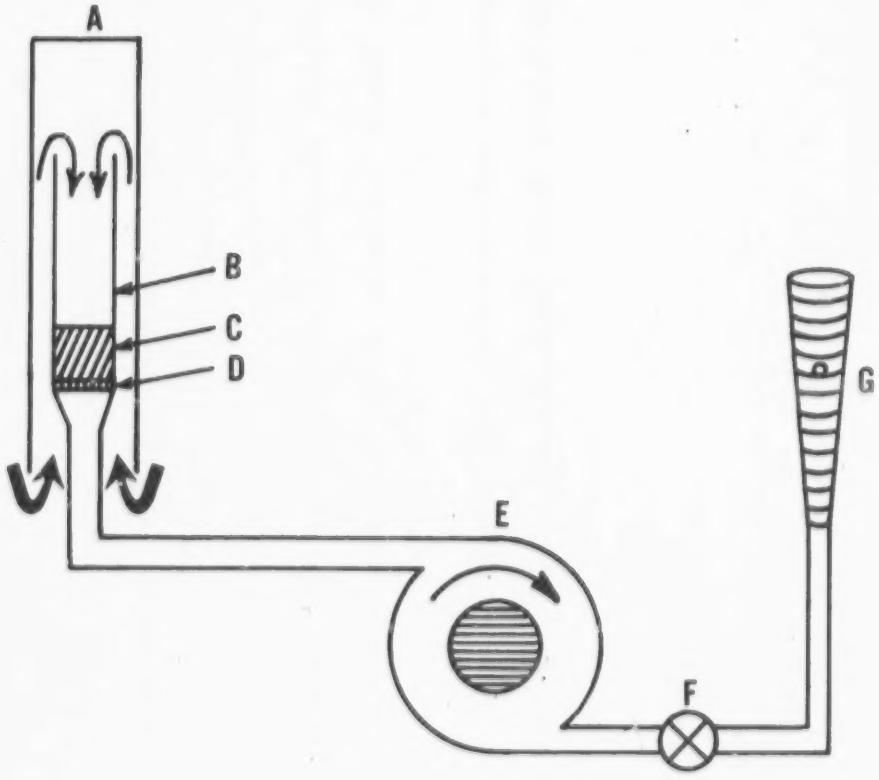
Vg = 1445 liters

$$CO\ ppm = 195$$

This CO level is far above the nominal daily average (10-50 ppm) which was reported in the NAPCA publication. Therefore, it also appears that PbO_2 can be used for ambient air sampling as well as for mobile and stationary sources. An additional feature of the PbO_2 sampler is that SO_x, CO, HCl, and possibly other pollutants can be determined on the same sample when the applicable analysis techniques are perfected.

Figure 1

SUGGESTED AIR SAMPLING DEVICE USING PbO_2 SORBENT



LEGEND:

A. HEATED COVER FOR PREHEATING AIR SAMPLE

B. PbO_2 CONTAINER

C. PbO_2 BED: 30/50 MESH, 8mm HIGH×25mm DIA.

D. FILTER TO RETAIN PbO_2

E. AIR PUMP

F. FLOW CONTROL VALVE

G. FLOW MEASUREMENT DEVICE

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